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SIGNED Frans Vaurio
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POWER SUPPLY AND CALIBRATION CIRCUIT FOR USE WITH UNBONDED STRAIN GAGES

INTRODUCTION

The unbonded type strain gage transducer has been used at the Institute for various force measurements such as the determination of the sealing strength of waxed paper, the coefficient of friction of treated and untreated papers, and the sealing strength of plastic coated paper. This report describes the structure and use of auxiliary equipment needed for recording forces detected with the strain gage.

At present we have two types of unbonded strain gages on hand. They are produced by the Statham Instruments, Incorporated, 254 Carpenter Road, Hato Rey, Puerto Rico. They are described by the manufacturer as follows:

Transducer Model No.	G1-4-250	G1-24-350
Serial No.	1892	5085
Range	± 4 oz.	± 24 oz.
Input Terminals:	1 and 4 (Green and Red)	1 and 4 (Green and Red)
Output Terminals:	2 and 3 (Black and White)	2 and 3 (Black and White)
Maximum Input Volts--E:	8	14
Input Resistance--R_{in}:	235.7	346.9 ohms
Output Resistance--R :	235.7	346.9 ohms
Calibration Factor--F:	580.2	112.1

The CALIBRATION FACTOR F is expressed as the open circuit output voltage in microvolts due to a unit input of the variable with one volt applied to the input terminals.

The strain sensitive resistance wire elements of the transducer are arranged in the form of a Wheatstone bridge. Either ALTERNATING OR DIRECT current may be used as the input, depending upon the requirements of the indicating or recording instrument.

POWER SUPPLY AND CALIBRATION CIRCUIT

The circuit shown in Figure 1 was developed after a little experimentation as a modification of the circuit suggested by the supplier for connecting a transducer to a power supply and indicator

The circuit involves the following features. The transformer is a step-down type (Minneapolis-Honeywell No. 15602-2 with 115 volt primary and 25 volt secondary) to give 25 volts at 16 volt-amperes. The alternating current is rectified with a 100 ma. Sarakasian selenium type rectifier model number 100. A 15,000 ohm 1 watt bleeder resistor and a 250 mfd. 25 volt d.c. electrolytic capacitor are used to smooth out the d.c. This combination gave 26 volts d.c.

It was decided to provide each gage with the proper maximum voltage and with connections which would minimize the possibility of error which might occur in connecting the different transducers.

A voltage divider circuit was devised as follows:

Assume that the maximum current drawn from the d.c. source will be 50 ma. with the 24 ounce strain gage in the circuit. Then

$$I_{max} = E/R = 26/R = 0.050$$

$$R = 520 \text{ ohms}$$

Since there is a limit of 40.3 ma. specified by the manufacturer on the current which can be safely passed through the strain gage, then, assuming 50 ma. will be drawn from the power supply, there must be 50 minus 40.3 or 9.7 ma. in the portion of the voltage divider which is in parallel with the transducer.

The specifications for the strain gage place a maximum of 14 volts across the strain gage input. This same voltage will be across the portion of the voltage divider which is in parallel with the strain gage. The resistance of the voltage divider which is in parallel with the strain gage must then be

$$R = 14/0.0097 \text{ or approximately } 1,445 \text{ ohms.}$$

The resistance of the loop circuit consisting of the strain gage and the portion of the voltage divider in parallel with it is then obtained from:

$$1/R_{loop} = 1/1,445 + 1/346.9$$

$$R_{loop} = 279.5 \text{ ohms}$$

Since the total resistance desired is 520 ohms (including the strain gage), then 520 minus 279.5 leaves 240.5 ohms must be placed in series with

the loop to complete the voltage divider. A 100-ohm potentiometer was included to give limited control of the gage voltage.

The voltage divider circuit for the ±4 ounce transducer was calculated assuming the same total voltage divider resistance. Then the effect of different resistance values in series with the 100-ohm potentiometer was calculated as in the following example:

$$1/R_{loop} = 1/(R_{pot.} + R_x) + 1/R_{strain\ gage.}$$

If we were to use 1000 ohms

$$1/R_{loop} + 1/(100 + 1{,}000) + 1/235.7$$

$$R_{loop} = 194 \text{ ohms.}$$

This would give a voltage of 6.47 volts across the strain gage. By plotting the resistance against the voltage, a curve was obtained and used to determine the resistance necessary to give the 8 volts desired. Since commercial standard resistors are not available in exactly the required values, a compromise was necessary. The circuit as used was determined by the resistors on hand.

A voltmeter is used to show the voltage being applied to the strain gage.

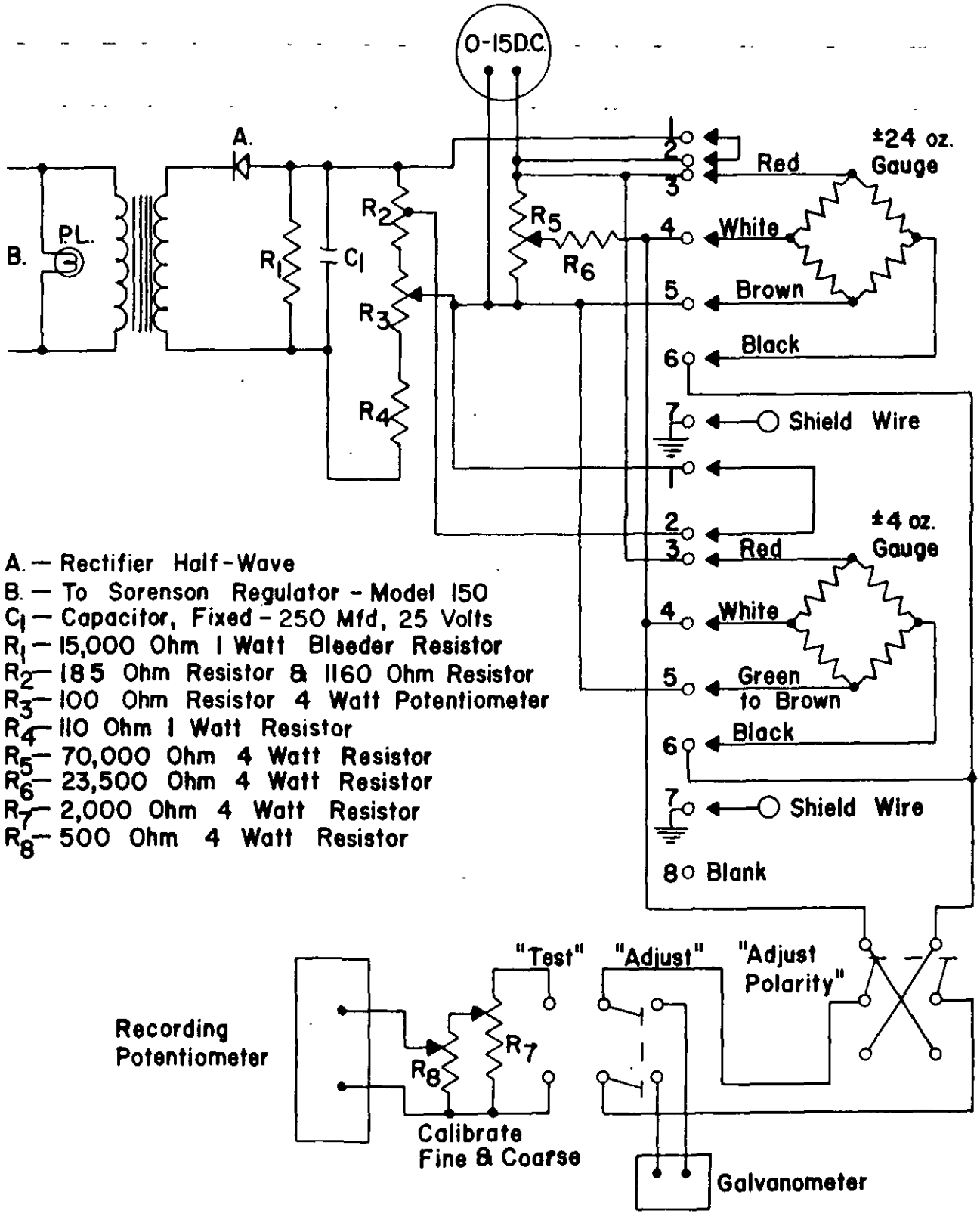
The zero adjustment of the strain gage cir cuit is accomplished with a 70,000 ohm potentiometer and a 23,500 ohm padder resistor.

A double-pole double-throw switch is used to adjust the polarity

if necessary. Another double-pole double throw switch is used to switch from Adjust to Test. The calibration of the recorder is accomplished by deadweight loading the strain gage and adjusting the calibration potentiometers. A "Coarse" and "Fine" adjust allows for precise control. The calibration is checked at two or more positions and a correction curve is prepared.

Each strain gage has its own cable and plug-in socket so that no mistakes will be made in booking them to the power supply. The gages should be used one at a time, however, to avoid overloading the power supply.

fv/mk



A. — Rectifier Half-Wave
B. — To Sorenson Regulator - Model 150
C_1 — Capacitor, Fixed - 250 Mfd, 25 Volts
R_1 — 15,000 Ohm 1 Watt Bleeder Resistor
R_2 — 185 Ohm Resistor & 1160 Ohm Resistor
R_3 — 100 Ohm Resistor 4 Watt Potentiometer
R_4 — 110 Ohm 1 Watt Resistor
R_5 — 70,000 Ohm 4 Watt Resistor
R_6 — 23,500 Ohm 4 Watt Resistor
R_7 — 2,000 Ohm 4 Watt Resistor
R_8 — 500 Ohm 4 Watt Resistor

Figure 1

PROJECT REPORT FORM

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COOPERATOR The Institute of Paper Chemistry
REPORT NO. 16
DATE August 5, 1955
NOTE BOOK 1271, pages 120-129, 133-
PAGE 135, 140-160 to Notebook 1108,
pages 20-27, 34, 39-52

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CYANOETHYLATION

INTRODUCTION

When cellulose is treated with acrylonitrile in the presence of a basic catalyst, such as NaOH, the acrylonitrile is linked to the cellulose in an ether type of bond.

$$\text{Cell} - OH + CH_2 = CH - CN \underset{\text{NaOH}}{\overset{H_2O}{\rightleftharpoons}} \text{Cell}-O-CH_2-CH_2-CN \qquad (1)$$

Reactions of this type have been carried to the trisubstituted stage per glucose C_6 unit.

These cyanoethylcelluloses have been hydrolized and used as thickening agents, sizing agents, and protective colloids. The making up of an alkali soluble product is as follows: (2)

Cellulose, in a finely divided state, is mixed with 20-30% NaOH solution. The amount of NaOH should be proportional to the cellulose calculated on the basis of the C_6 glucose unit. To this is added 0.2 - 0.5 mole equivalents of acrylonitrile per C_6 glucose unit. At 20-30°C. the reaction begins to take place.

Thus the alkali soluble cyanoethylated product is formed and such solutions can be precipitated by acidification or neutralization.

Recently the partial cyanoethylation of cotton has created a new type of textile with qualities such as: (3)

(1) Resistance to micro-organism attack.

(2) Resistance to wet and dry heat degradation.

(3) Good receptiveness to all classes of dyes, and including acid dyes.

(4) Abrasion resistance higher than normal cotton fabric.

There is some indication that the moisture regain for samples containing 1-5% N is less than for normal cotton.

The above mentioned qualities would probably be desirable in a paper product. The fact that moisture regain goes down as nitrogen content rises above one per cent might indicate that a paper partially cyanoethylated would not expand or swell as much as an untreated paper, when exposed to damp atmospheric conditions.

A sample pulp submitted by the Institute of Paper Chemistry was cyanoethylated by the Monsanto Chemical Company. As stated in a letter to Dr. Howells dated March 21, 1955 from Monsanto Chemical Company, the preparation of these pulps was carried on in the following manner:

"The material to be treated was received in sheet form."
These sheets were Weyerhaeuser bleached sulfite pulp sent

out by the Institute of Paper Chemistry. "To help in handling it was cut into approximately 1-1/2" squares with a paper cutter. One pound of these pieces was placed in a 10-liter flask which contained 8 liters of acrylonitrile. The flask was submerged in a constant temperature bath and was provided with a high speed mechanical stirrer and a thermometer. This material was left to soak overnight. The following day the stirrer was activated and the bath heated. When the desired temperature was reached one pound of 2% aqueous sodium hydroxide solution was added. The reaction was allowed to go for a given time and then an equivalent amount of acetic acid was added to neutralize the caustic catalyst. The cyanoethylated pulp was then transferred to beakers and unreacted acrylonitrile separated by filtration. The product was then washed with water until no acrylonitrile could be detected and the wash water was neutral to litmus paper. The cyanoethylated pulp was then dried in the sun.

Several runs were made following the same procedure except that time, temperature, and caustic concentration were varied. The following table shows the conditions used and results obtained:

Time, Min.	Temp., °C.	Concentration of Caustic Solution	Percent Nitrogen
25	35	2%	1.85%
40	35	4%	3.43%
94	45	4%	5.10%
180	57	4%	8.65%

Since it was necessary to combine several runs to obtain large samples, the products of two similar runs were placed in a 5-gallon jar half filled with water. The mixing was accomplished by using a Lightnin' mixer for one hour. The excess water was removed by filtration and the product was again dried in the sun. The electric motors used for stirring during the reaction and mixing periods were 1/3 h.p. units, the reaction unit rotating at approximately 1000 r.p.m. The mixing unit was a 3" four-bladed propeller turning at approximately 1725 r.p.m."

In their letter Monsanto Chemical Company mentioned that in their tests on cyanoethylated papers they had achieved as much as a tenfold increase in sizing as measured by standard ink penetration tests, as compared with handsheets made with the same pulp which had not been cyanoethylated. The cyanoethylated pulps mentioned had a percentage of nitrogen between four and seven.

The cyanoethylated products containing 3.43% N and 8.65% N were tested as papermaking fibers. These pulps as well as an untreated control were beaten for various lengths of time, then handsheets were formed and tested. As the percentage of nitrogen--a measure of the degree of cyanoethylation-- went up, the strength of the paper decreased. The data is represented in Figures 1 and 2. It is seen from the freeness curve, Figure 3, that although the 3.43% N sample behaved much the same as normal paper, the 8.65% N has its own characteristic curve. This again would

Figure 1

The Effect of Cyanoethylation on Bursting Strength

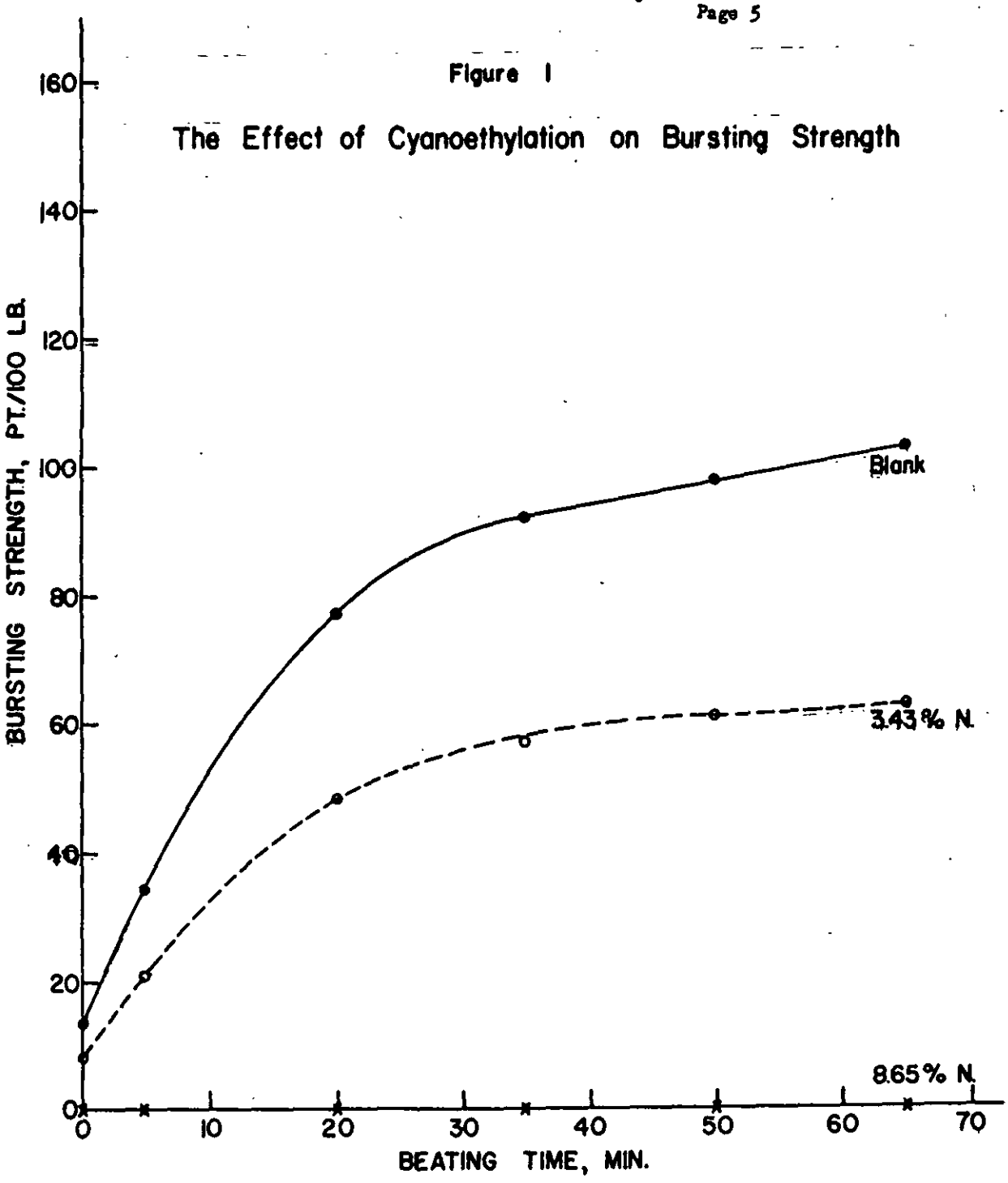


Figure 2

The Effect of Cyanoethylation on Tear Factor

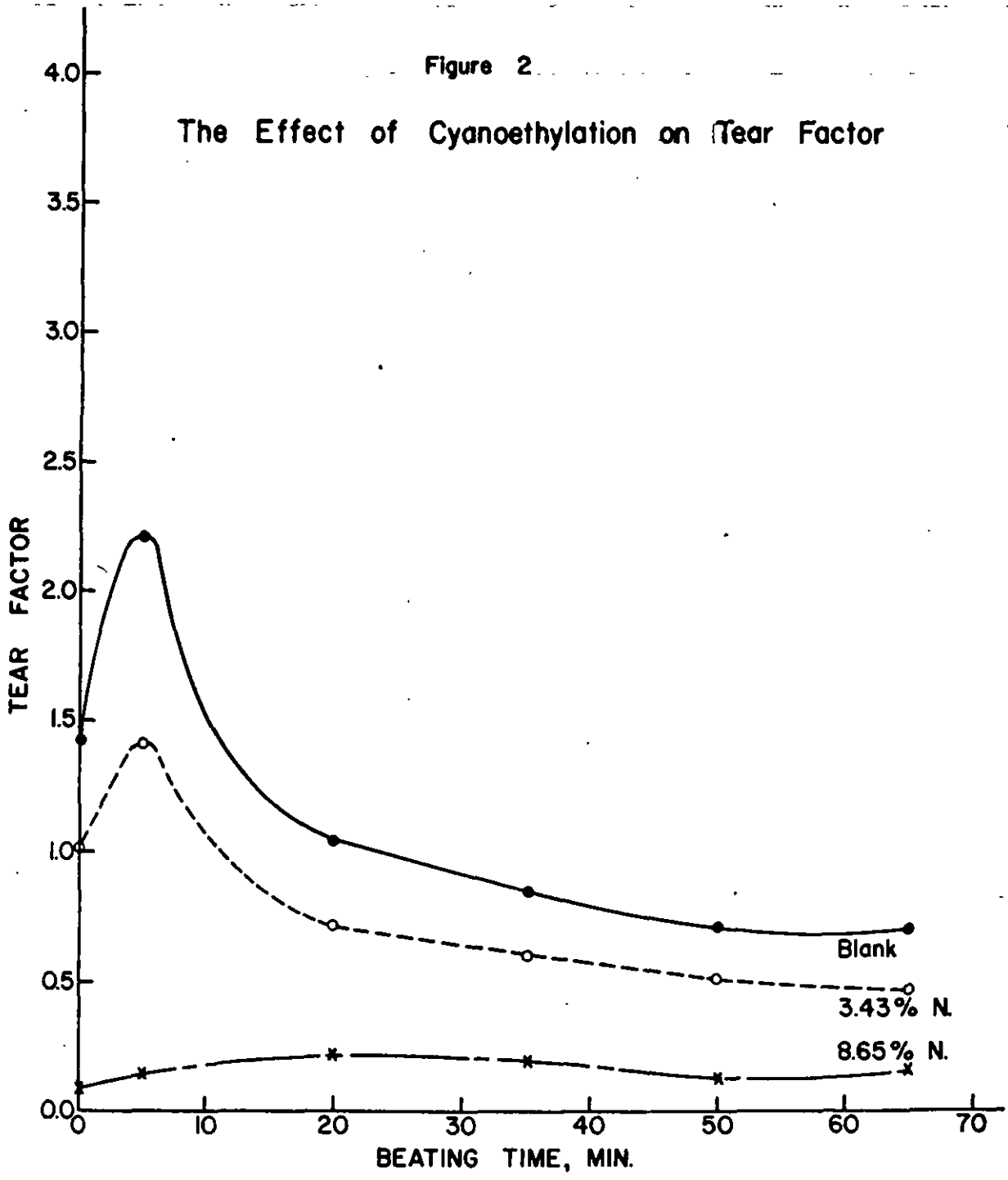
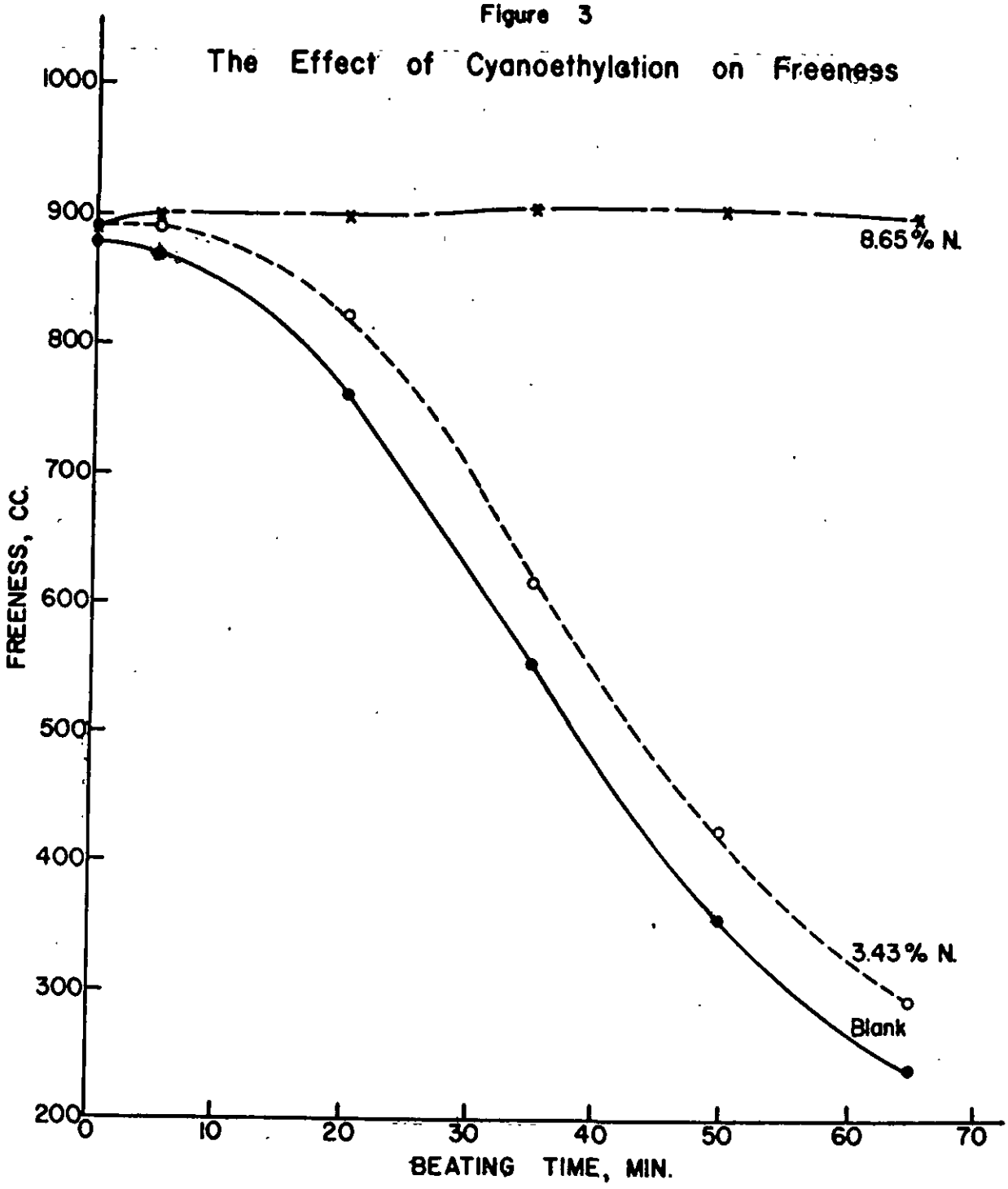


Figure 3

The Effect of Cyanoethylation on Freeness



indicate that water has less and less effect on the paper as the percentage of cyanoethylation is raised.

The lack of strength of the paper might be due to several things:

1. Lack of good bonding between fibers
2. A shortening of fiber
3. Weakening of the fiber by treatment used.

Ordinary cotton fabric when cyanoethylated has about the same strength as untreated cotton. However, strength increases have been obtained and these increases depend more on the method of cyanoethylation than on the degree. (3) Ordinary cellulose fiber is not changed in strength in up to 5% N content. Thus it would seem that points one and two above are the primary weakening cause.

The extent to which fibers have been shortened is an important one since, when all factors are the same, the tensile strength of the sheet will vary as $\sqrt[2]{L}$, where L is the weighted average fiber length. The tear will vary as $L^{3/2}$. These things hold true if the diameter does not decrease with decrease in fiber length. (4) The width of the cyanoethylated fiber, if it follows the example of cotton, will increase. (3)

PROCEDURE

From the introduction it is evident that cyanoethylation of pulp by the Monsanto method has weakened the sheets that are formed from these pulps. Therefore several courses of action present themselves:

A. A treatment of the already cyanoethylated pulps to try to make them stronger.

B. Investigation of the cyanoethylated pulps for factors other than those already made to see if cyanoethylation affords some good points.

C. Lamination of weakened cyanoethylated sheet to other sheets and thus add strength and perhaps get a sheet with good surface characteristics.

D. Cyanoethylation of preformed sheets to improve surface characteristics and still retain the strength of the sheet.

E. Cyanoethylation of pulps by different methods.

Trials at improving the strength of sheets were made by several methods. Some pulp samples were given a sodium hydroxide treatment. Others were treated with alum. Handsheets were made in all cases without neutralization of the caustic or alum. The treatments were all carried out at room temperature by stirring the pulp in the sodium hydroxide solution for one hour.

In the sodium hydroxide treatment several reactions are possible:

1. $\text{Cell-O-CH}_2\text{-CH}_2\text{-CN+2H}_2\text{O} \xrightarrow{\text{NaOH}} \text{Cell-O-CH}_2\text{-CH}_2\text{-COOH+NH}_3$

2. $\text{Cell-O-CH}_2\text{-CH}_2\text{-CN} \xrightarrow[\text{heat}]{\text{NaOH}} \text{Cell-O-Na} + \text{polyacrylonitrile}$ (5)

Since cyanoethylation is an equilibrium reaction, there may be some monomer of acrylonitrile and some cellulose formed. The monomer may react with

water thus,

$$2\ CH_2 = CHCN + H_2O \longrightarrow O\ (CH_2CH_2CN)_2$$

Hydrolysis of the cyanoethylated pulp probably would not occur to any great degree at room temperature in one hour for it has been found that a sample of cloth originally containing 2.88% N had 2.36% N at the end of one hour if treated with a solution containing 2.0 oz. NaOH/gal. of solution at 120°F. Only 0.06% remained after heating the cyanoethylcellulose for one hour at 160°F. in the sodium hydroxide. (6)

In an attempt to give the cyanoethylated pulps strength, the treated pulps were mixed with an equal amount of Weyerhaeuser pulp. It was hoped that the Weyerhaeuser pulp would contribute strength while the cyanoethylated pulp would perhaps make the sheet abrasive and water resistant. Handsheets were made as follows:

All pulps were beaten for 35 minutes at a consistency of 1.57 and a bedplate pressume of 5500 gm. Foaming in the cyanoethylated pulps was bad, and Dow Antifoam A was used in these beater runs. The beaten pulp was diluted to half its consistency by water or NaOH, as the case might be. In the sodium hydroxide treatment 1 hour was allowed for mixing time. Four thousand ml. of water was run into the Valley ($8\frac{1}{2}$ x $8\frac{1}{2}$-inch) square sheet mold. About 400 ml. of pulp (enough to make an 8x8-inch sheet of 2.49 g.) was used per sheet.

Couching was accomplished by placing two blotters on the sheet

and the couch roll was placed in the center and rolled back and forth four times. Damp blotters were used wherever possible to prevent the hygroexpansivity of the blotter from changing the characteristics of the sheets. However, at times the handsheets had so much affinity for the screen that the use of damp blotters was impossible.

The sheets were pressed between blotters at 100 lb. for 3 minutes, dried at about 225°F. for 2 minutes with the wireside on the drum, then for another 3 minutes with blotters removed. Sheets were prepared as per Table I.

TABLE I

Pulp	Treatment	Method of Removal from screen
Weyerhaeuser	None	Damp blotters
"	1.5% NaOH	" "
"	3.75% NaOH	" "
"	1.5% $Al_2(SO_4)_3$	" "
1.85% N	None	" "
"	1.5% NaOH	" "
"	3.75% NaOH	Dry blotters
"	1.5% $Al_2(SO_4)_3$	Damp blotters
"	Equal amount of Weyerhaeuser	" "
5.10% N	None	Dry blotters + vacuum
"	3.75% NaOH	" " + "
"	Equal amount of Weyerhaeuser	Damp blotters

These samples were sent for the following tests: basis weight, caliper, apparent density, tensile, stretch, tear, erasurability, hygroexpansivity, and Clark softness.

Several samples of pulp were sent for a fiber classification. This was done to see whether a change in fiber lengths could account for some of the decrease in strength of the sheets as formed from the cyanoethylated pulp. The results of the fiber classifications are in Table II. Due to difficulty in dispersing these cyanoethylated pulps, the sampling as made in the Clark Classifier might have been in error.

TABLE II

Clark Classifier

Pulp - 4.924 g. Ovendry Weyerhaeuser

Screens	Grams		%	
	Run A	Run B	Run A	Run B
on 14	2.189	2.090	44.46	43.18
Through 14 on 30	1.807	1.796	36.10	37.11
" 30 " 50	.426	.483	8.65	9.99
" 50 "100	.353	.339	7.17	7.00
Total	4.775	4.708	98.98%	97.28%

Pulp - Monsanto Cyanoethylated to 3.43% N

Run A 5.010 g. Ovendry Run B 5.024 g. Ovendry

on 14	2.634	2.412	52.57	48.01
Through 14 on 30	1.271	1.307	25.37	26.01
" 30 " 50	.569	.395	11.36	7.86
" 50 " 100	.366	.369	7.30	7.34
Total	4.840	4.483	96.60%	89.22%

Pulp - Monsanto Cyanoethylated to 5.10% N 5.002 g. Ovendry

on 14	2.511	50.20
Through 14 on 30	1.244	24.87
" 30 on 50	.378	7.56
" 50 on 100	.359	7.18
Total	4.492	89.81

As set out in Table II large fibers increased in per cent of total fibers recovered and a decrease in recovery occurred between 14 and 30-mesh screens. If the results indicate the distribution of the cyanoethyl group, then it would seem that the large fibers were more heavily cyanoethylated. However, this indication may be in error since there was some evidence that the cyanoethylated pulps were not well dispersed. Because of the inconclusive results and because it was also felt that a cross sectional analysis should be made, samples of Weyerhaeuser 1.85% N, 3.43% N, and 8.65% N pulps were sent for a length-to-cross sectional analysis by microscope.

Laminations of sheets were made by sandwiching a Weyerhaeuser sheet between two cyanoethylated sheets. Here the Weyerhaeuser sheet was meant to give strength, while the cyanoethylated material might give good surface characteristics.

Treatment of preformed sheets was another method of attack. The first experiment in this phase was done in the following manner. Sheets of kraft, alpha cellulose, sulfite, and rag paper were dipped in 1.0% sodium hydroxide, then in acrylonitrile--all at room temperature. The sheets were dried in an oven at approximately 60°C. The boiling point of acrylonitrile is 71-72°C. Thus the oven was hot enough to provide energy of activation for the cyanoethylation reaction but not quite hot enough to drive the acrylonitrile off instantly. The sheets were found to be dry in approximately 5 minutes, but were allowed to remain in the oven for 10 minutes. A weight gain analysis

was made but the percentage of cyanoethylation was so small, if any, that this simple treatment did not appear to be enough for cyanoethylation and a system for refluxing the paper in acrylonitrile was developed.

An alternate method of treatment by dipping sheets in acrylonitrile and then in caustic was also tried.

The higher temperature treatment of cyanoethylation under refluxing conditions seemed best for at 55°C. about 3.8% N is affixed to cotton only after heating for an hour, while at 71-72°C. as much as 5% N can be affixed to cotton in two to three minutes. (3) The reaction rate at 55°C. is represented in Figure 4.

Since the reaction time was between 3 and 5 minutes in the oven, as set out in Figure 4, it might be assumed that between 0.2% N to 0.8% N might be affixed to the treated sheets.

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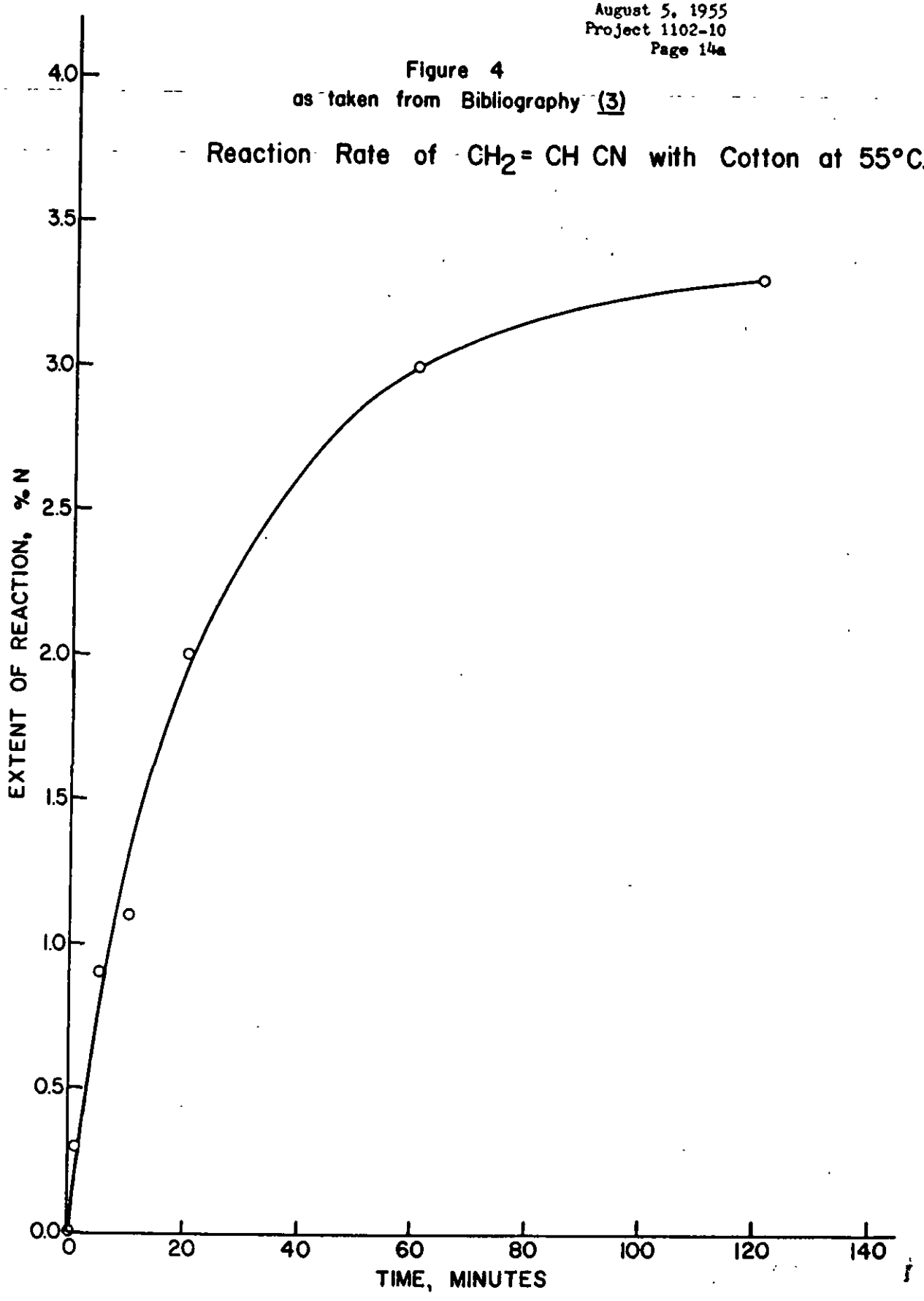
Figure 4
as taken from Bibliography (3)

Reaction Rate of $CH_2 = CH\ CN$ with Cotton at 55°C.



RESULTS OF HANDSHEETS

The methods of preparation of sheets in Table III has previously been described. The numbered code refers to the notebook, the page and sample number on that page.

As can be seen from Table III, the Weyerhaeuser control had the greatest tear factor. The strength, as indicated by tear factor, went progressively down as the per cent nitrogen was increased. Treatment of the pulps with NaOH before handsheet formation lowered the tear factor in every case. As the concentration of NaOH was raised, the tear factor was lowered with one exception--that being the treatment of Weyerhaeuser from 1.5% NaOH to 3.75% NaOH. The results indicated that the sodium hydroxide treatment did not improve the tear strength of cyanoethylated paper as indicated by tear factor.

The Baldwin-Southwark tensile was highest for the pulp containing 1.85% Nitrogen. However, the basis weight was slightly higher in this sample than in the control and 5.10% N paper. Thus the most that can safely be said is that there was no evidence that tensile was lowered for the lower percentage nitrogen sheets. The next highest tensile was in an equal mixture of 1.85% nitrogen pulp and Weyerhaeuser. Sodium hydroxide lowered the tensile strengths with one exception--the tensile of an untreated to 5.10% nitrogen paper treated with 3.75% NaOH. However, here again basis weight might have been the answer for this.

TABLE III*

RESULTS OF PAPERS MADE FROM CYANOETHYLATED PULP, WEYERHAEUSER BLEACHED SULFITE

Code Number	Description of paper	Basis Weight lb. 25x40/500	Apparent Density	Tear Factor	Schopper Fold	Clark Softness	Baldwin-Southwark Tensile, lb./inch	Baldwin-Southwark Stretch, %	Abrasion Rate, mg./stroke	Hygroexpansivity, % Change from 65-50% R. H.
1271-127-A	Weyerhaeuser control	45.3	10.5	1.41	231	2.11	15.8	3.2	.180	0.120
1271-133-1A	Weyerhaeuser cyanoethylated to 1.85% Nitrogen	47.1	9.6	1.02	608	2.14	19.3	4.3	.077	0.145
1271-134-2A	Weyerhaeuser cyanoethylated to 5.10% Nitrogen	45.2	9.6	0.49	7	3.18	8.6	1.9	.095	0.080
1271-127-B	Weyerhaeuser treated with 1.5% NaOH	47.4	10.3	1.22	215	1.84	14.7	2.7	.220	0.115
1271-133-1B	1.85% N pulp treated with 1.5% NaOH	48.3	10.7	0.79	643	2.20	17.4	3.3	.055	0.145
1271-127-C	Weyerhaeuser treated with 3.75% NaOH	43.5	9.5	1.36	64	2.07	13.4	2.5	.203	0.105
1271-133-1C	1.85% N pulp treated with 3.75% NaOH	43.8	10.0	0.78	766	2.66	13.0	2.6	.055	0.170

TABLE III*(Continued)

RESULTS OF PAPERS MADE FROM CYANOETHYLATED PULP, WEYERHAEUSER BLEACHED SULFITE

Code Number	Description of paper	Basis Weight, lb. 25x40/500	Apparent Density	Tear Factor	Schopper Fold	Clark Softness	Baldwin-Southwark Tensile, lb./inch	Baldwin-Southwark Stretch, %	Abrasion Rate, mg./stroke	Hygroexpansivity, % Change from 65-50% R.H.
1271-134-2C	5.10% N treated with 3.75% NaOH	47.8	10.2	0.48	9	2.94	8.7	1.5	.092	0.105
1271-127-D	Weyerhaeuser treated with 1.5% $Al_2(SO_4)_3$	47.8	10.4	1.32	139	1.94	15.5	2.9	.090	0.115
1271-133-1D	1.85% N pulp treated with 1.5% $Al_2(SO_4)_3$	45.7	9.9	0.92	327	2.48	15.6	3.7	.088	0.150
1271-133-1E	Equal amounts of Weyerhaeuser and 1.85% N pulp	52.4	10.5	1.13	632	1.53	17.7	3.7	.093	0.145
1271-134-2E	Equal amounts of Weyerhaeuser and 5.10% N pulp	45.5	10.3	0.75	42	2.57	13.0	2.7	.088	0.115

* The data in this Table, except for Abrasion Rate, comes from Project 1684, Memorandum dated April 25, 1955, Institute File Numbers 163050 to 163061. The abrasion rate was calculated from curves of weight loss in mg. plotted against total number of strokes. These curves were obtained directly from the Humidity Room. Samples were conditioned at 50% R.H. and 73°F.

Alum lowered the tensile strength of the 1.85% nitrogen sheet, but not to as great an extent as that of standard Weyerhaeuser.

Schopper fold was increased approximately 2.6 times in a 1.85% nitrogen cyanoethylated sheet over the Weyerhaeuser control. The 5.10% nitrogen containing sheet decreased to 1/33 the folding strength of the Weyerhaeuser control. The folding strength dropped for the Weyerhaeuser control as it was treated with caustic and alum. The caustic treatment of the 1.85% nitrogen containing sample improved its already high fold endurance, but alum treatment lowered it. However, the lowest folding strength of the 1.85% sheet was higher than the high of the Weyerhaeuser samples. Sheets made from an equal mixture of Weyerhaeuser standard pulp and pulp cyanoethylated to 1.85% nitrogen had a fold endurance slightly higher than even untreated 1.85% N paper.

Abrasion tests were made on some of the sheets by erasing a 3x3-inch area at a vertical force of 555 gm. The number of strokes was plotted against milligrams of paper removed. The slope is a measure of the abrasion rate in mg. removed per stroke. These graphs are shown in Figures 5 to 9. Here again the sheets containing 1.85% nitrogen excelled the sheet containing only Weyerhaeuser and that containing 5.10% nitrogen. Alum treatment had an adverse effect on abrasion resistance, but its effect was by far the greatest on sheets made from standard Weyerhaeuser. Sodium hydroxide seems to have been beneficial to the cyanoethylated pulps, but decreased the abrasion resistance of the Weyerhaeuser standard. Sheets made from a mixture of 5.10% N pulp

Figure 5

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)

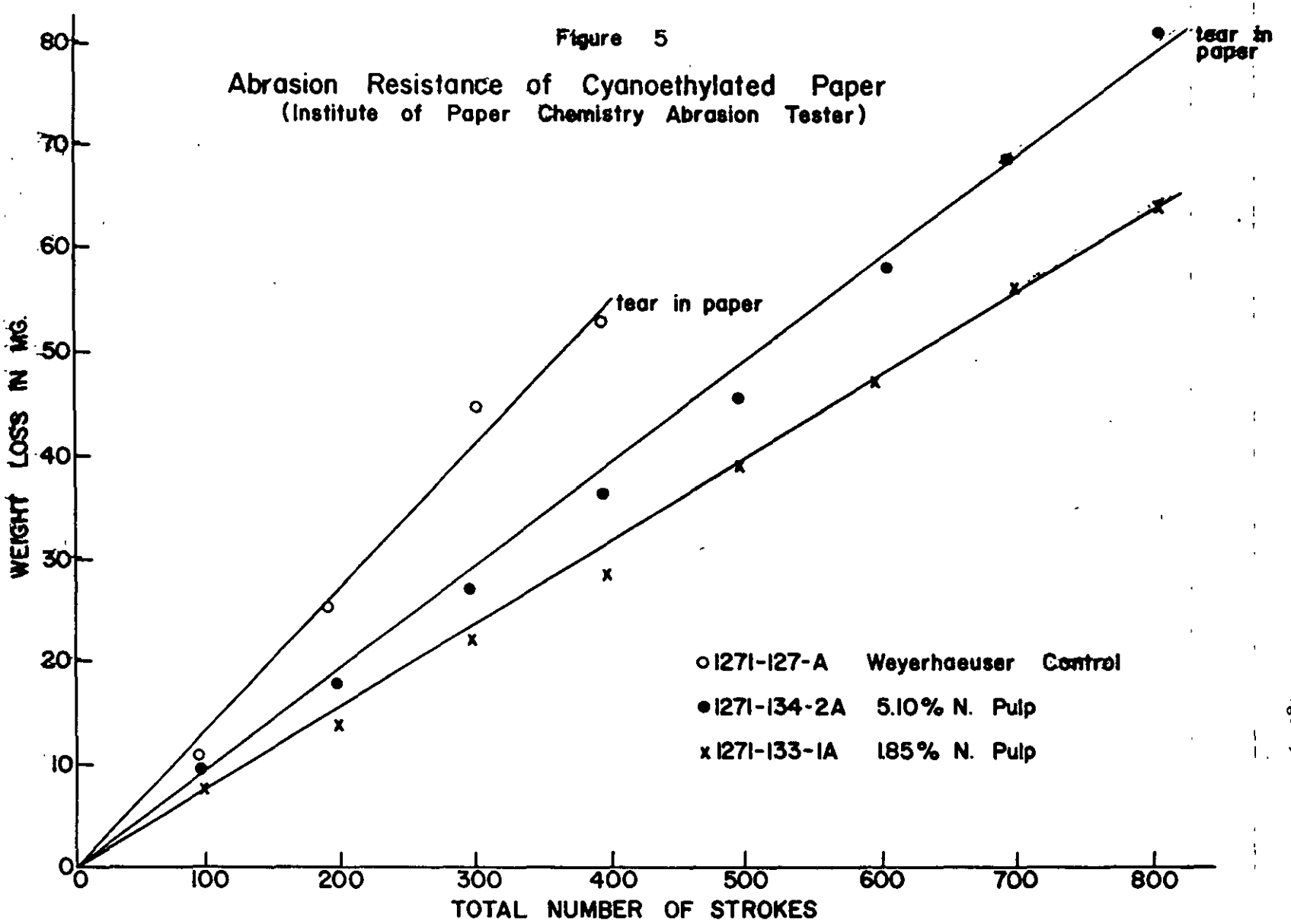


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Figure 6

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)

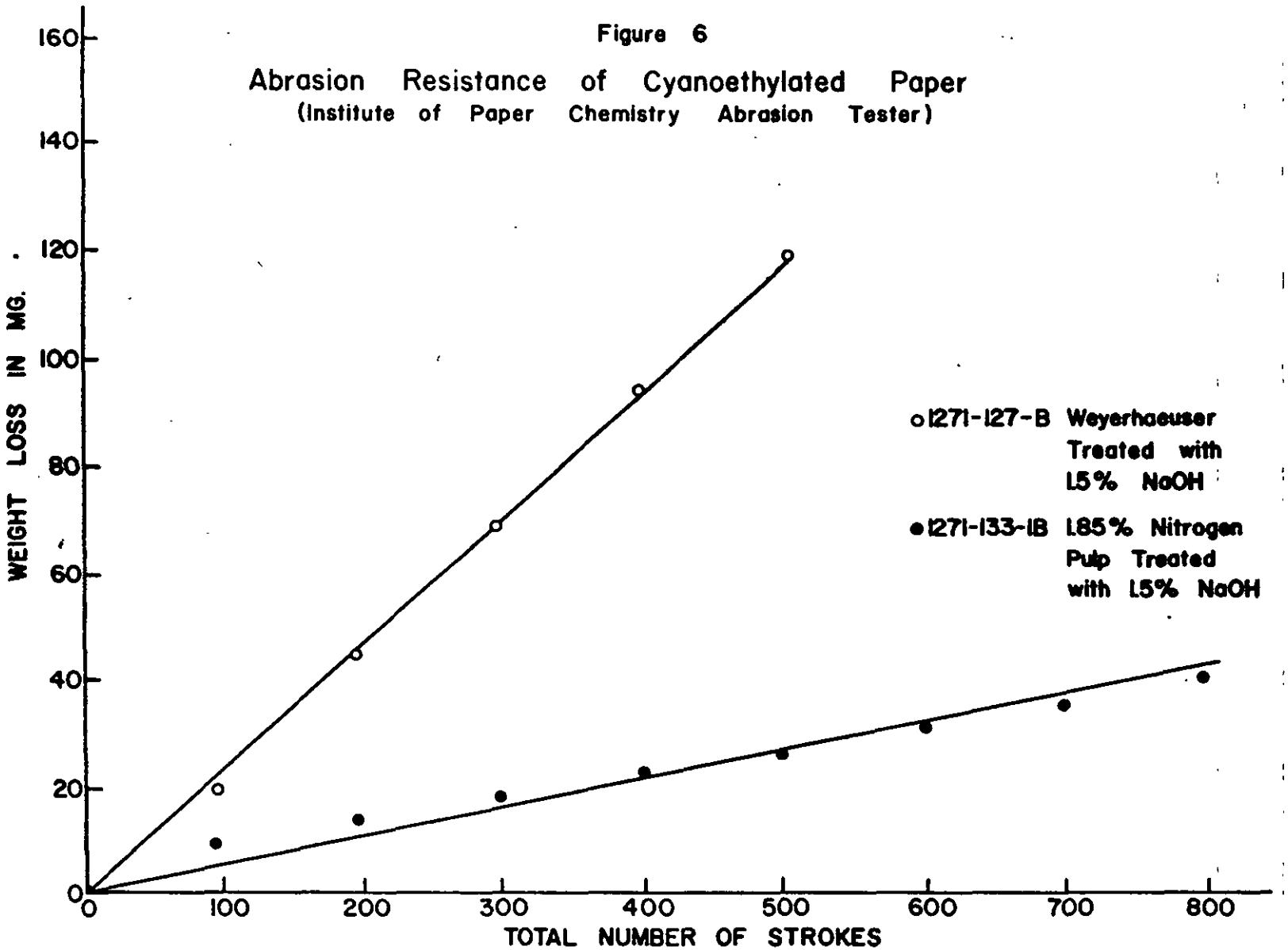

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Figure 7

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)

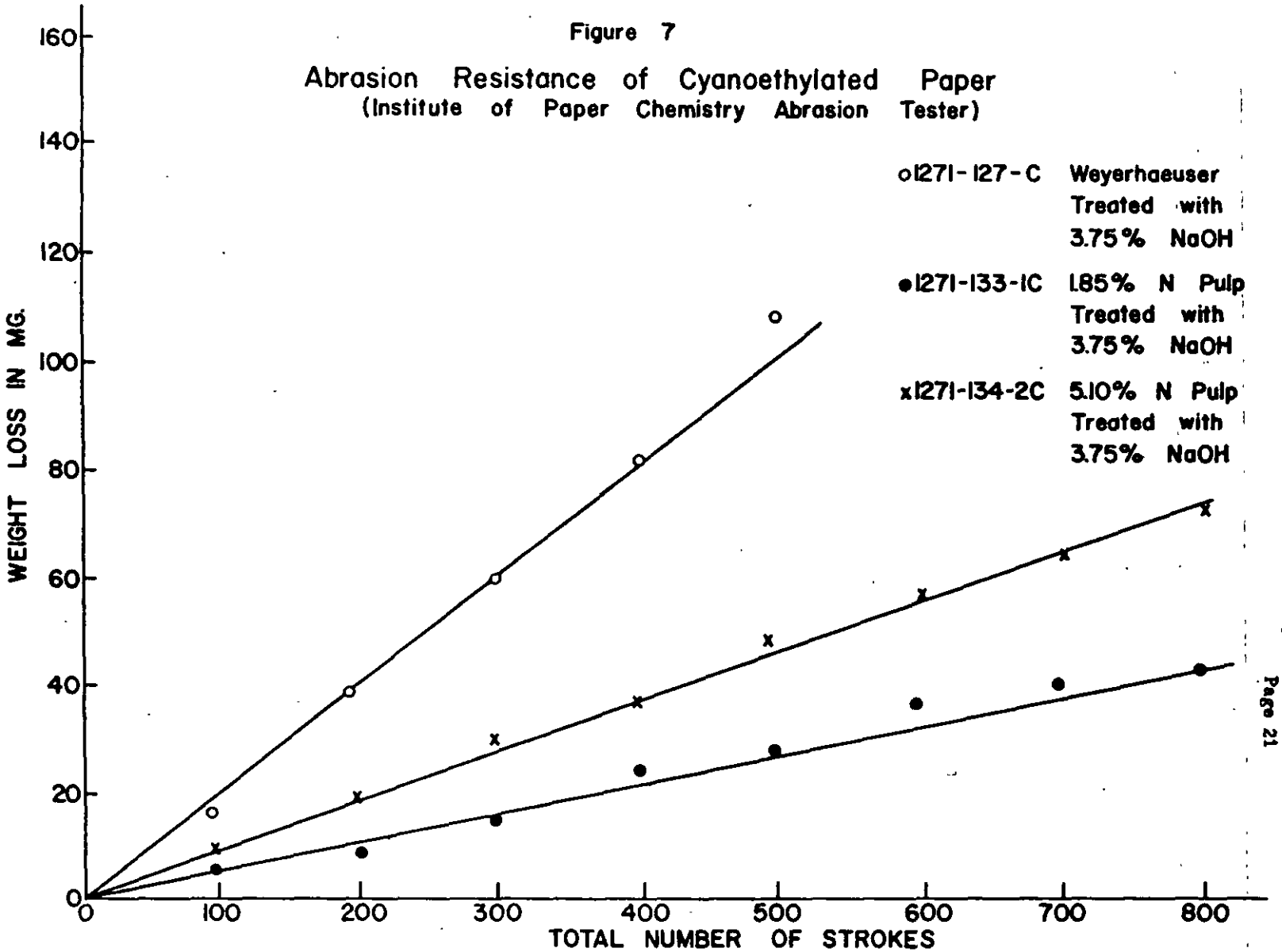

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Figure 8

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)

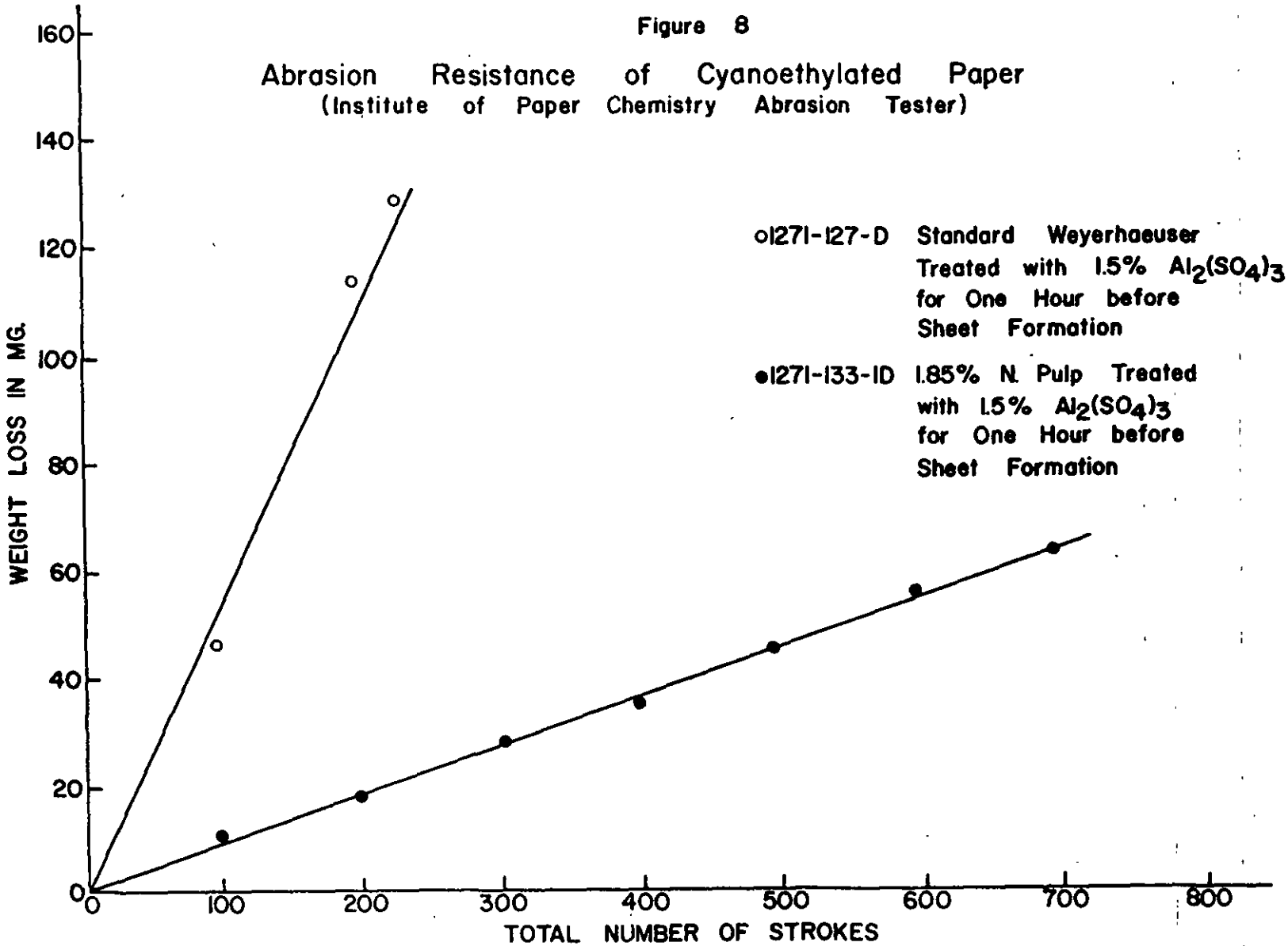
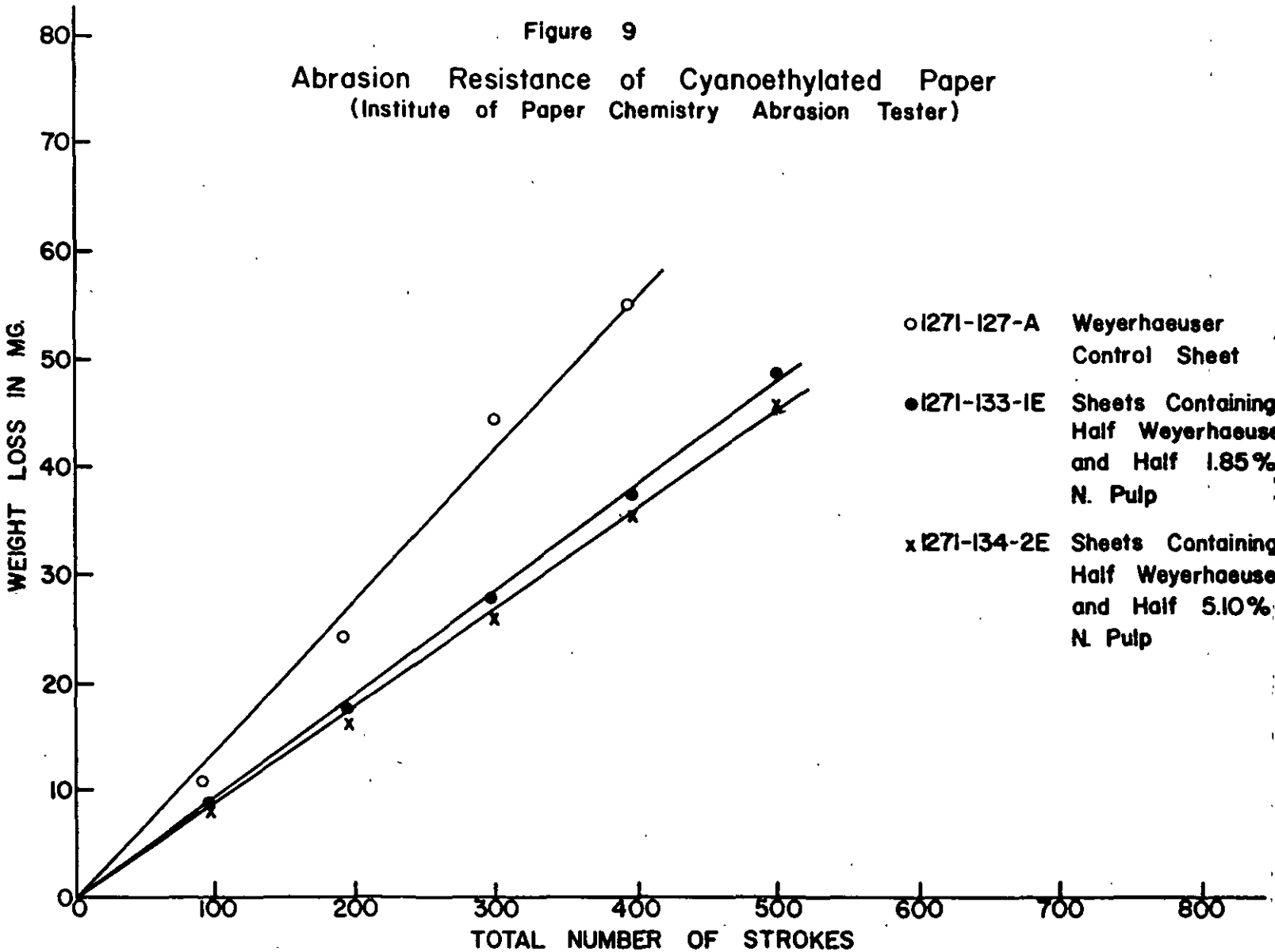


Figure 9

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)



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and an equal amount of Weyerhaeuser pulp showed a higher resistance to abrasion than a 50 to 50 ratio of 1.85% N and Weyerhaeuser. Both were more resistant to abrasion than Weyerhaeuser standard.

Heat degradation tests were made on some of the cyanoethylated papers and the results are in Table IV. The sheets were subjected to 150°C. for 112 hours. This was a much more severe test than prescribed in the Institute methods (105°C. for 72 hours) and is similar to degradation used in cloth. (3) As can be seen, cyanoethylation protected the sheets somewhat. However, to try to compare the Schopper Folds in per cent degraded in this case would perhaps lead to erroneous conclusions since the undegraded sheets vary to such a great extent. In the 5.10% nitrogen containing sheet even though the original folding strength was low, the final strength was not much lower and was well within the range of possible error in the test since a minimum of 4 and a maximum of 8 were averaged to obtain the value for the degraded paper. The mixed pulps were considerably weakened. The weakening was of the same order as for the Weyerhaeuser control. Basis weight seems to have increased by degradation indicating some oxidation of the papers.

Hygroexpansivity, as seen in Table III, increases somewhat with a small percentage of nitrogen and then decreases. Sodium hydroxide reduced the hygroexpansivity of the control but increased it for the cyanoethylated pulps. Alum showed the same effect as NaOH. Mixing untreated pulp with an equivalent of treated pulp increased hygroexpansivity.

The tear factor decreased with cyanoethylation. Figures 10 and 11

TABLE IV *

RESULTS OF HEAT DEGRADATION TESTS

Code Number	Description of Sheets	Basis Weight, lb. 25x40/500	Tear Factor	Schopper Fold	Baldwin-Southwark Tensile, lb./inch
1271-127-A	Weyerhaeuser control	45.3	1.41	231	15.8
1108-22-W	Heat degraded Weyerhaeuser	45.7	0.37	1	11.5
1271-133-1A	Cyanoethylated Weyerhaeuser to 1.85% N	47.1	1.02	608	19.3
1108-22-1W	Heat degraded Weyerhaeuser cyanoethylated to 1.85% N	51.4	0.47	5	13.4
1271-134-2A	Cyanoethylated Weyerhaeuser to 5.10% N	45.2	0.49	7	8.6
1108-22-2W	Heat degraded Weyerhaeuser cyanoethylated to 5.10% N	46.0	0.39	6	7.7
1271-133-1E	1.85% nitrogen pulp + equal amount of Weyerhaeuser	52.4	1.13	632	17.7
1108-22-1W2	Heat degraded Weyerhaeuser cyanoethylated to 1.85% N + equal amount of Weyerhaeuser	51.1	0.47	2	13.6

TABLE IV * (Continued)

RESULTS OF HEAT DEGRADATION TESTS

Code Number	Description of Sheets	Basis Weight, lb. 25x40/500	Tear Factor	Schopper Fold	Baldwin-Southwark Tensile, lb./inch
1271-134-2E	5.10% nitrogen sample + equal amount of Weyerhaeuser	45.5	0.75	42	13.0
1108-22-2W2	Heat degraded Weyerhaeuser cyanoethylated to 5.10% nitrogen + equal amount of Weyerhaeuser	44.3	0.36	2	10.4

* Data was obtained from Project 1684, Memorandum dated May 6, 1955, Institute File No. 163450-54, and Memorandum dated April 25, 1955, Insti tute File Nos. 163050, 163054, 163058, 163059, and 163061.

show almost linear relationships. The folding strength was somewhat increased by cyanoethylation as was the abrasion resistance. These increases, however, were dependent on the degree of cyanoethylation, and it appears that a maximum in these factors could be obtained by controlling the degree of cyanoethylation. The data indicated that cyanoethylated pulp might have good aging qualities as illustrated by a lesser degree of heat degradation of the 5.10% nitrogen pulp over the others. Of course, the 5.10% nitrogen sample possessed such little tear resistance that it is probably impractical, but perhaps somewhere between 2 and 5% nitrogen-containing pulps might have sufficient strength and yet show good aging qualities. However, per cent nitrogen might be only one factor involved. The method of cyanoethylation might also be a factor to be considered since several positions are open on a cellulose molecule to the cyanoethylated group.

Several of the cyanoethylated pulps were sent for a microscopic fiber classification. Before sending these samples we were faced with the task of dispersing the fibers. The 1.85% nitrogen pulp, cyanoethylated by Monsanto, was not too difficult to disperse in water; however, ordinary stirring was not enough to disperse the higher nitrogen content pulps (3.43% and an 8.65%). Consequently the Waring blender was used. The higher the per cent nitrogen, the more hydrophobic the samples seemed to be. Such solvents as acetone, tetrahydrofuran, carbon tetrachloride, and Methyl Cellosolve acted more readily than water on the more cyanoethylated pulps. This fact might be of considerable importance in any future experiments since it has been proven

Figure 10

The Effect of Cyanoethylation on Tear Strength
(Pulp Treated by Monsanto, Beaten 35 Minutes)

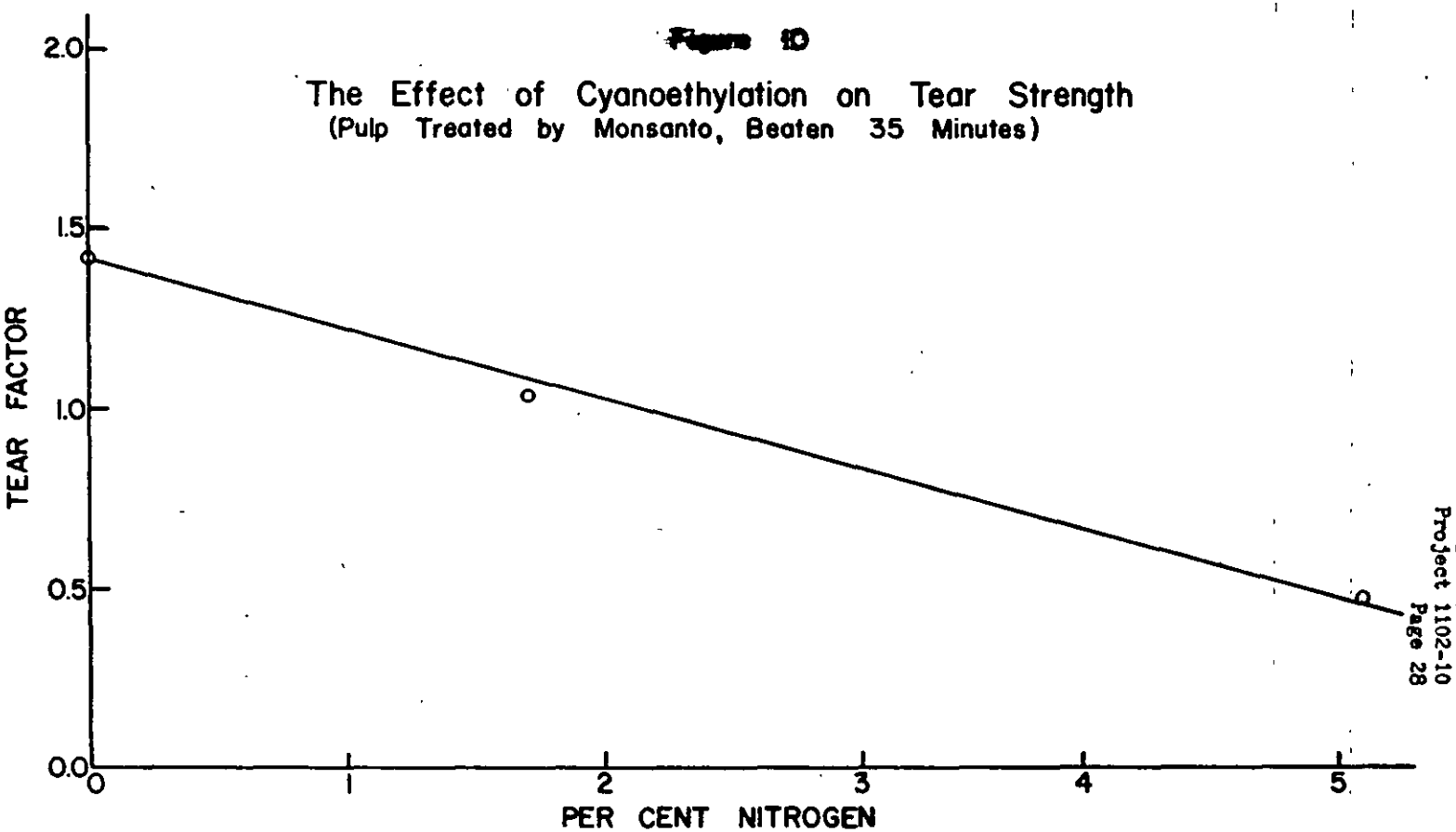

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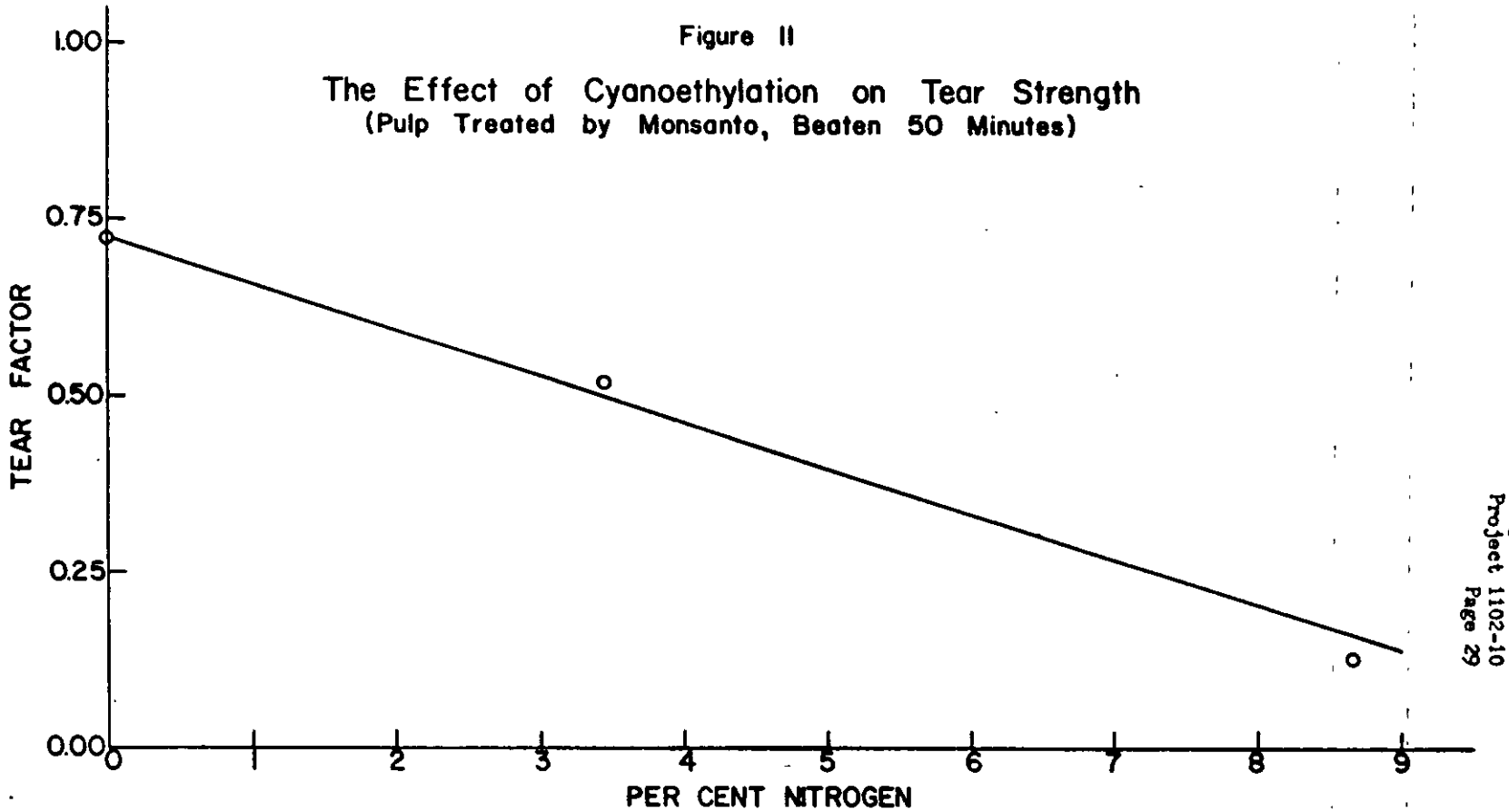
Figure II

The Effect of Cyanoethylation on Tear Strength
(Pulp Treated by Monsanto, Beaten 50 Minutes)



that the hydrophilic character of fiber surfaces determine to a large extent the bonding of fibers.(7) Perhaps a mere dipping of the sheet in these chemicals after formation might change the properties of the cyanoethylated papers for the better.

The following reaction was proposed for improving tear resistance:

$$CH_2O + H_2O + 2CH_2 = CH\text{-}CN \xrightarrow{H_2SO_4} (CH_2 = CHCONH_2)_2\ CH_2 \qquad (8)$$

However, concentrated sulfuric acid (85%) is required as a catalyst. This concentrated acid proved to be too great--the paper dissolved after short treatments.

The arithmetic average fiber length did not indicate a progressive shortening of fibers as the degree of cyanoethylation was increased. In general, the weighted average fiber length did decrease. The data obtained from the microscopic analysis of cyanoethylated fibers is represented in Table V. (9) According to TAPPI T 233 sm-53, the tear strength of a sheet is proportional to $L^{3/2}$, where L is the weighted average fiber length. The curve of L against per cent nitrogen had a negative slope indicating that L may be a factor in the decrease in tear strength. Figure 12.

A portion of the tear strength loss might also have been due to the decreased fiber-to-fiber bonding because of the hydrophobic cyanoethyl group and also the hydroxyl blocking caused by the cyanoethyl group.

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7. Use of Beater and Headbox Additives for the Improvement of Sheet Characteristics. Jack E. Jayne, John C. Tongren and Donald T. Jackson, Tappi 33, Jan. 1950, p. 32
8. Magot, E. E., Faris, B. F., Reith, J. E., Salisbury, L. F., Acid Catalized Reactions of Nitriles. Journal of American Chemical Society, Vol. 73, p. 1028; 1951.

TABLE V

EFFECT OF CYANOETHYLATION ON SIZE OF FIBERS

Code Number	Description of Sheets	Arithmetic Average Fiber Length, mm.	Weighted Average Fiber Length, mm.	Average Fiber Width, mm.
1271-157-A	Weyerhaeuser control, unbeaten	0.925	2.34	0.032
1271-142-1	1.85% N pulp unbeaten; put through blender	0.990	1.90	0.029
1271-142-2	3.43% N pulp unbeaten; put through blender	1.26	2.27	0.036
1271-142-3	8.65% N pulp unbeaten; put through blender	0.969	1.85	0.028
1271-157-B	1.85% N pulp unbeaten	0.804	1.90	0.028

9. Project 1684, Memorandum dated April 25, 1955, pp. 1-7; Institute File Nos. 162655, 162657, 163126, 163202, 163205.

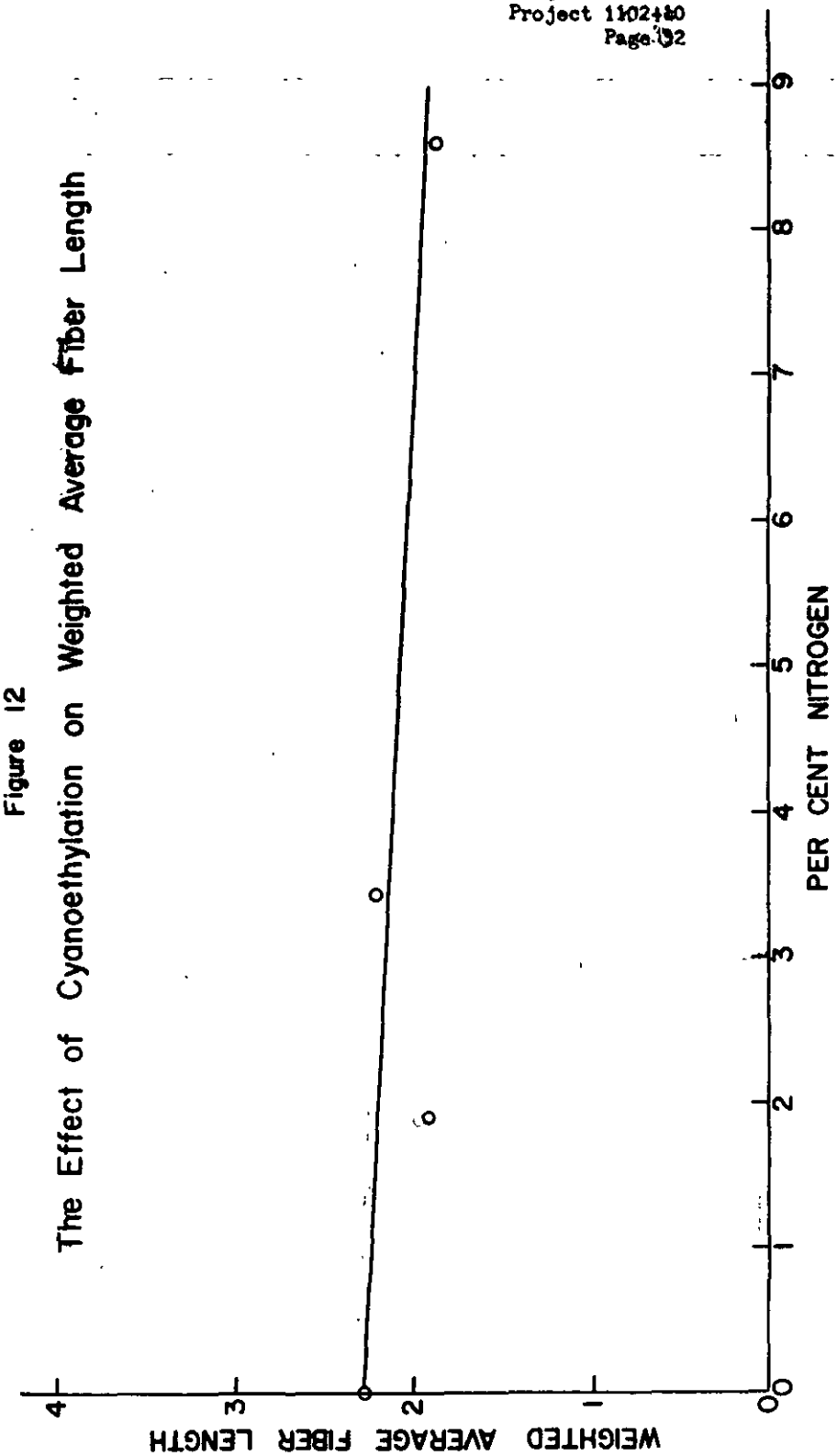


Figure 12

The Effect of Cyanoethylation on Weighted Average Fiber Length

It is entirely possible that the caustic treatment as it was used for its catalytic effect on cyanoethylation may have leached out some part of the fiber. Since the method of cyanoethylation by Monsanto was not available to use at the time of these experiments, we were not able to perform blank caustic treatment of Weyerhaeuser pulp to determine its effect on the fiber. However, indications from the tests performed were that caustic did decrease tear resistance somewhat.

Laminations of sheets were made utilizing various weights of 5.10% nitrogen paper to sandwich Weyerhaeuser control sheets of various weights. The sheets were wet-pressed to each other and dried on a drum drier. Results of the tests made are in Table VI. In general, tear factor was reduced as the weight of 5.10% N sheets was increased. Tensile showed no definite trend, nor did % stretch. Hygroexpansivity showed a trend toward decreasing as the amount of laminated cyanoethylated paper was increased. This is quite an odd point in that the hygroexpansivity seemed to be related to the stresses and strains in the sheet. That is, since the inner sheet in each lamination had a greater degree of hygroexpansivity, increasing the proportion by weight of the inner sheet in each case made for greater hygroexpansivity of the laminated sheets.

TABLE VI *

CHARACTERISTICS OF PAPER SURFACED WITH CYANOETHYLATED FIBER

Code Number	Description of paper	Basis Weight, lb. 25x40/500	Caliper, inch	Apparent Density	Tear Factor	Clark Softness	Baldwin-Southwark Tensile, lb./inch	Baldwin-Southwark Stretch, %	Hygroexpansivity, % Change from 65-50% R. H.
1271-146-F	Weyerhaeuser (8x8 in.-0.83 g.) sandwiched in two (8x8 in.-0.83 g.) 5.10% N sheets	42.3	0.0043	9.8	0.66	3.40	11.7	2.1	0.100
1271-146-G	Weyerhaeuser (8x8 in.-2.49 g.) sandwiched in two 5.10% N (8x8 in. - 0.83 g.) sheets	68.9	.0060	11.5	0.90	1.05	21.9	2.6	0.120
1271-146-H[illegible]	Weyerhaeuser (8x8 in.-1.75 g.) sandwiched in two 5.10% N (8x8 in. - 1.20 g.) sheets	[illegible]	0.0066	11.8	0.83	0.853	24.6	3.2	0.105
1271-146-I	Weyerhaeuser (8x8 in.- 0.83 g.) sandwiched in two 5.10% N (8x8 in. - 1.66 g.) sheets	72.6	0.0063	11.5	0.76	0.973	21.4	2.7	0.090

* The data in this table taken from Project 1684, Code Office Memorandum dated April 25, 1955 and August 5, 1955, Institute File No. 163092, 163093, 163094, 163095. Samples were conditioned at 50% R. H. and 73°F.

Erasurability tests of the laminates were made, the results of which are in Figures 13-16. Of the samples tested 1271-146-H was the only sample that showed a break in the abrasion curve. However, this sample did not contain the least amount of cyanoethylated paper as a covering and this result may have been due to poor sheet formation. Some of the other samples which were abraded even to 1400 strokes did not show breaks in the abrasion curve. Dyeing tests made on these abraded sheets indicated that in sample 1271-146-H the cyanoethylated cover sheet was not completely abraded so that a complete change to the rate of abrasion of Weyerhaeuser untreated paper was not shown; samples 1271-146-G and 1271-146-F were about to have an abrasion rate change. The proof of this can be found from the following examples--the red being cyanoethylated, and the blue being Weyerhaeuser uncyanoethylated sheets. The dye solution used was a mixture of 0.100 g. Calcomine Blue DR and 0.100 g. Calcomine Scarlet 3B in 400 ml. demineralized water; 40 ml. of this dye were used per gram of paper in the dyeing. The paper was boiled in this dye mixture for 5 minutes, rinsed and dried.

1271-146-F

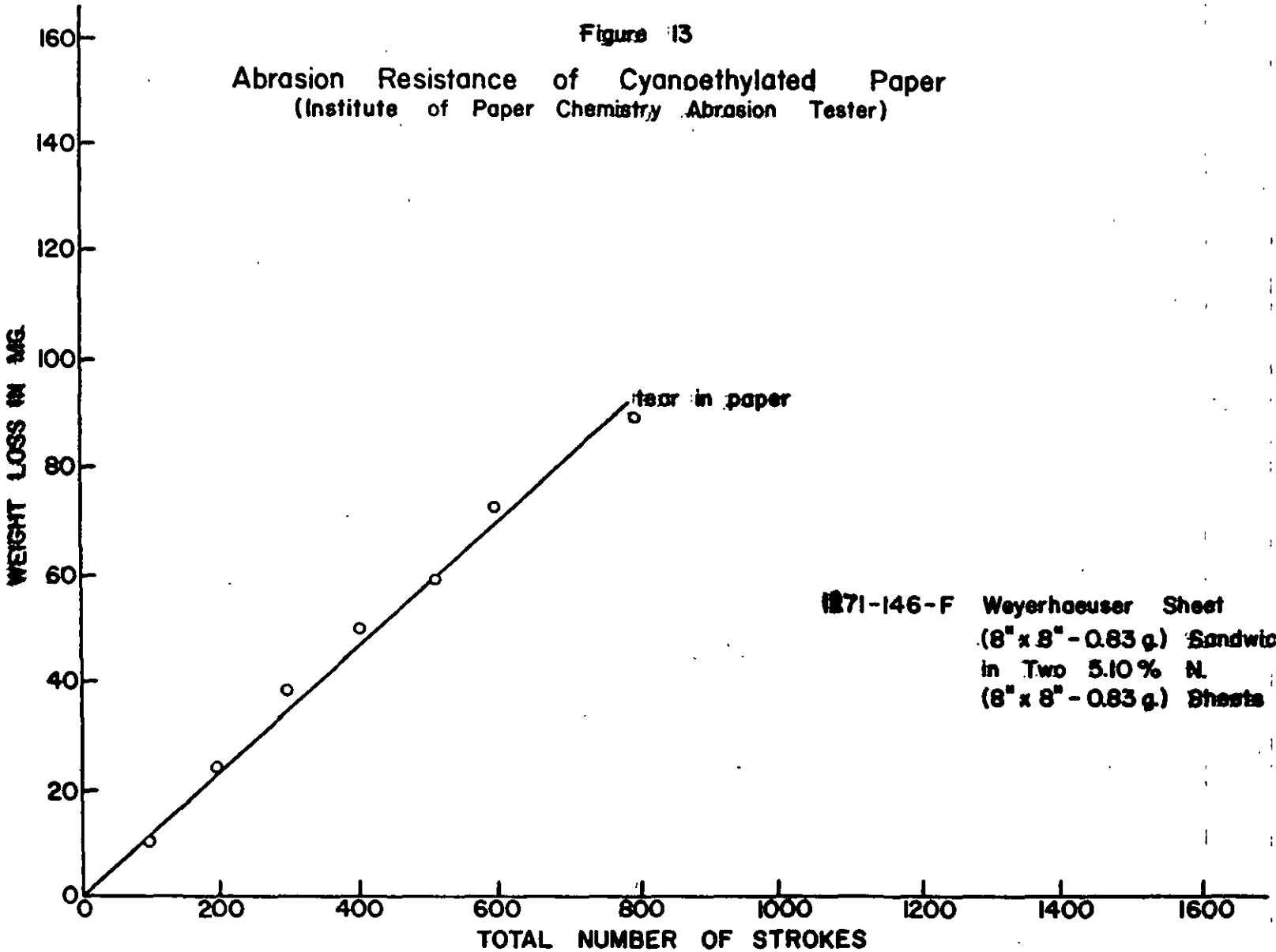
1271-146-H

1271-146-G

1271-146-I

Figure 13

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)



1871-146-F Weyerhaeuser Sheet
(8" x 8" - 0.83 g.) Sandwiched
in Two 5.10 % N.
(8" x 8" - 0.83 g.) Sheets

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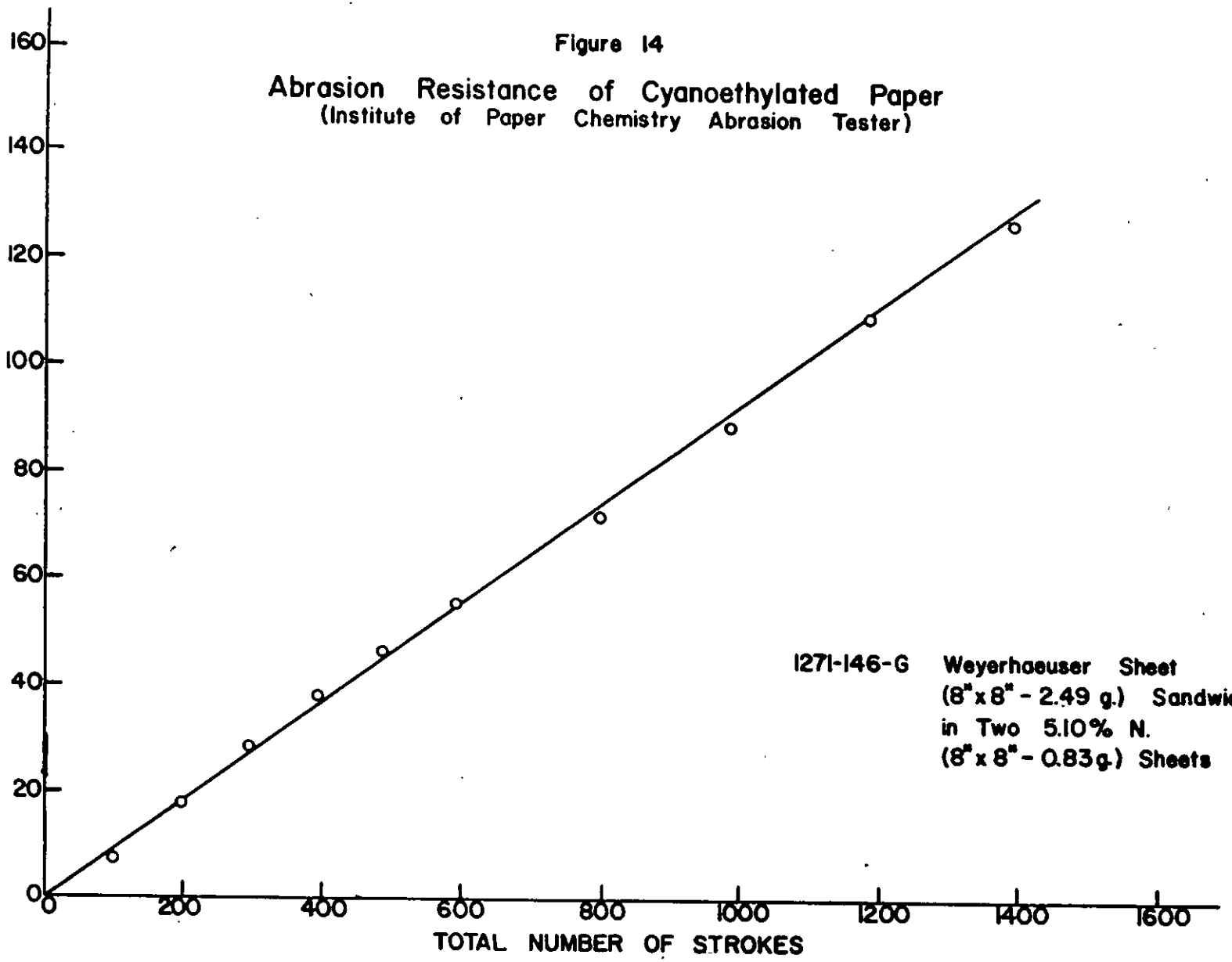
Figure 14

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)



1271-146-G Weyerhaeuser Sheet
(8"x8" - 2.49 g.) Sandwiched
in Two 5.10% N.
(8"x8" - 0.83g.) Sheets

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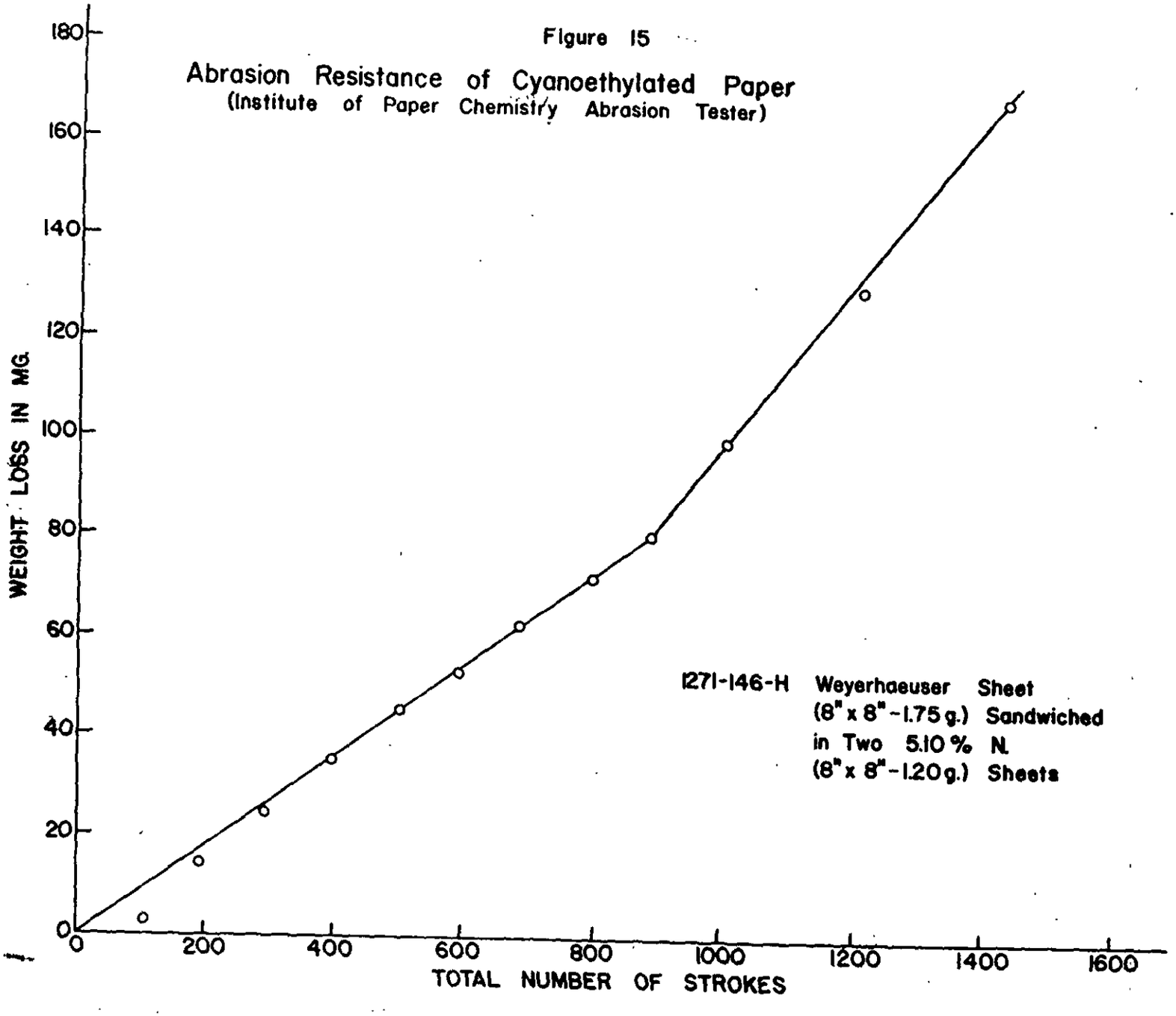
Figure 15

Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)



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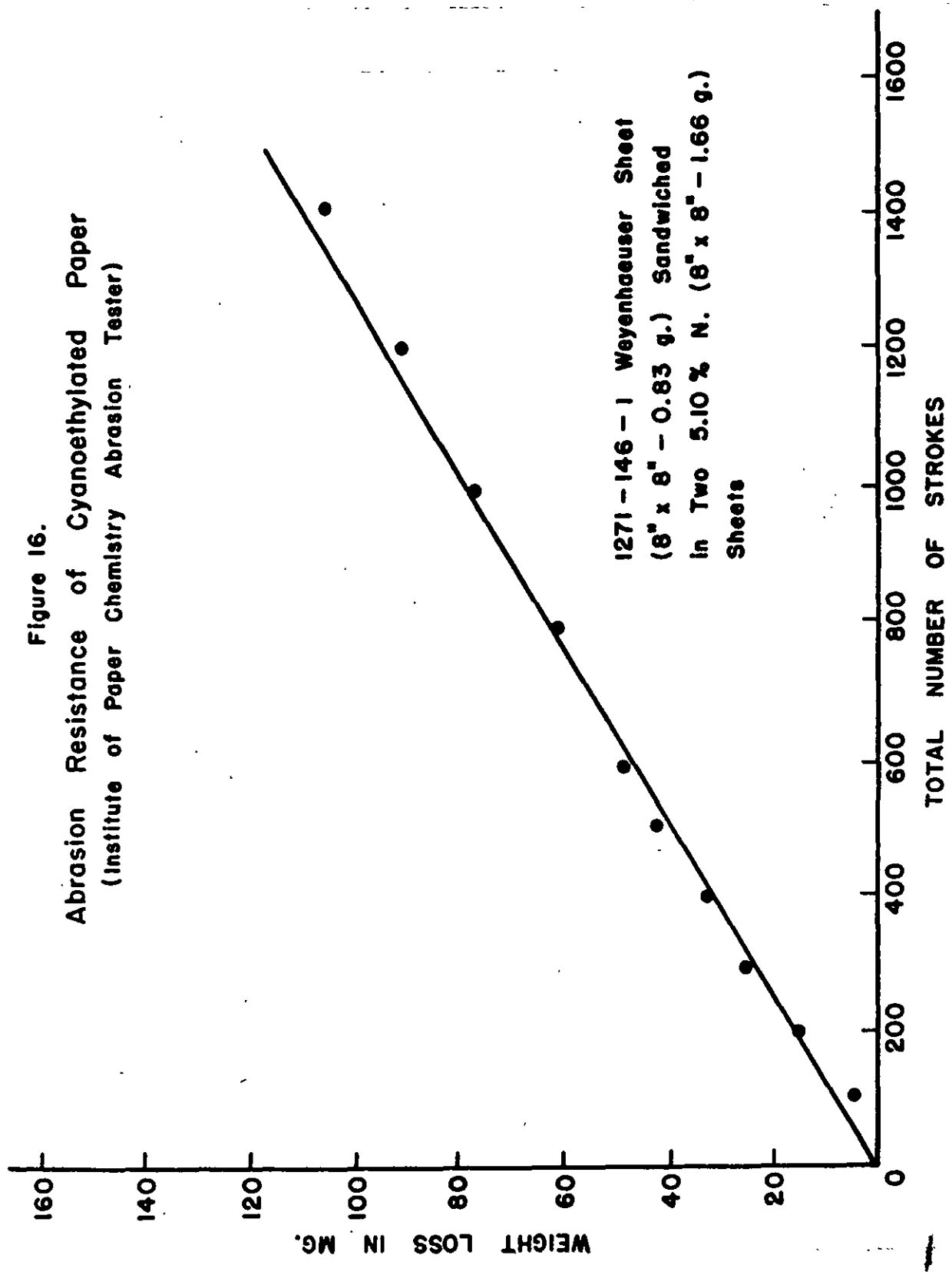

Figure 16.
Abrasion Resistance of Cyanoethylated Paper
(Institute of Paper Chemistry Abrasion Tester)

Cyanoethylations of preformed webs have been made. This treatment was tried by normal dipping operations as previously mentioned. However, dyeing tests showed that little or no acrylonitrile was reacted with the paper.

For this reason a reflux type treatment was developed for cyanoethylation. A waterleaf sulfite, a kraft, and a rag paper were cyanoethylated. The reactions were carried out at 35°C. in a mixture of 2,350 ml. acrylonitrile and 500 g. 4% NaOH. The cyanoethylation was terminated by addition of an amount of glacial acetic acid equivalent to the sodium hydroxide. The vessel was drained and the paper washed with water. Of the three papers treated, the kraft seemed to be least damaged by the drastic treatment. In fact, the kraft seemed to have been waterproofed to some extent in that it did not soak through in water even after several minutes. However, it could by no means be considered a size since ink feathered. The sulfite paper also withstood the cyanoethylation quite well. The rag paper, however, appeared not to be able to endure the moist conditions of the treatment and was considerably torn and roughed by our apparatus. Rinsing these sheets thoroughly with water after cyanoethylation was difficult and traces of alkalis, acids, or salts may have been left in the sheets. Upon heat degradation the cyanoethylated rag and sulfite paper webs were turned brown. However, the heat treatment given was quite harsh. The analytical laboratory indicated that, even in overnight heating at 105°C., as much as 30% of the cyanoethylation nitrogen was given off by the sulfite and rag papers. This may be due to inadequate removal of acid or base from these samples.

Or perhaps the nitrile is oxidized or otherwise attacked at high temperature even in the absence of ions.

Table VII contains some of the data received on the cyanoethylated machine papers. In each case cyanoethylation has reduced strength. The data obtained for heat degradation did not indicate in this case that cyanoethylation was of any value. An untreated rag paper seemed to withstand the degradation of heat to the greatest extent.

The Baldwin-Southwark percentage stretch increases with cyanoethylation. This was also the case with the sheets made from cyanoethylated pulps from the Weyerhaeuser to the 1.85% nitrogen-containing pulp. Softness of the paper made from pulps in each case increased with cyanoethylation. This was probably due to the lower bonding strength in the sheets. However, the surfaces of sheets made from cyanoethylated Weyerhaeuser were quite hard.

TABLE VII*

MACHINE PAPER TESTS

Code Number	Description of Paper	Nitrogen, %	Basis Weight, lb. 25x40/500	Caliper, Inches	Apparent Density	Elmendorf Tear g./sheet		Tear Factor		Baldwin-Southwark Tensile, lb./inch		Stretch, %		Schopper Fold	
						In	Across	In	Across	In	Across	In	Across	In	Across
1271-125-1	Waterleaf Rag Control, Fox River Paper Corp.	0.22	35.2	0.0030	11.7	51	54	1.45	1.53	14.1	7.4	2.4	5.0	109	27
1271-160-3A	Cyanoethylated rag	3.32	42.6	0.0042	10.1	34	54	0.80	1.27	6.9	3.8	3.5	8.2	10	4
1108-22-1R	Heat degraded rag control	- -	36.6	- -	- -	15	17	0.41	0.46	11.9	5.5	-	-	2	3
1108-22-2R	Heat degraded cyanoethylated rag	- -	39.2	- -	- -	8	-	0.20	-	0.6[a]		-	-	Broke under 1 kg. tension	
1271-121-1	Kraft control	0.20	55.4	0.0069	8.0	116	145	2.10	2.62	33.7	12.4	2.3	3.4	2440	334
1271-160-3B	Cyanoethylated kraft	4.84	75.7	0.0099	7.6	91	112	1.20	1.48	23.0	5.3	3.0	4.9	- -	- -
1271-124-1	Sulfite control	0.076	28.7	0.0030	9.6	24	27	0.836	0.941	21.0	10.1	2.3	4.6	226	63
1271-160-3C	Cyanoethylated sulfite	3.41	33.6	0.0036	9.3	23	29	0.68	0.86	12.7	5.9	3.6	8.6	87	13
1108-22-1S	Heat degraded sulfite control	- -	27.3	- -	- -	5	4	0.18	0.15	7.9	4.2	-	-	0	0
1108-22-2S	Heat degraded cyanoethylated sulfite	- -	29.8	- -	- -	-	-	-	-	2.3	0	-	-	0	-

[a] It was not possible to identify the machine direction of these tensile strips.

* The data in this Table comes from Project 1684, Institute File No. 160380, 160383, 160384, Code Office Memo dated December 22, 1954; Institute File No. 163415-163420, Code Office Memo dated May 4, 1955; Institute File No. 163446-163449, Code Office Memo dated May 6, 1955; Institute File No. 163510-163512, Code Office Memo dated April 26, 1955; Institute File No. 163416, 163418, 163420, Code Office Memo dated June 14, 1955 and April 27, 1955. Samples conditioned at 50% R.H. and 73°F.

The cyanoethylated machine paper had lower abrasion rates in each case due to cyanoethylation. This can be seen quite readily from Figures 18-20. This is the reverse of what occurred in the sheets made from cyanoethylated pulp.

From Table VII it can be seen that, although cyanoethylation did not decrease the Elmendorf tear seriously in the across direction of the papers--except for the kraft, the tear factor decreases due to an increase in basis weight. Cyanoethylation decreased the Elmendorf tear for the sulfite and rag paper in the "in" direction much more than in the "across" direction. This fact might have some particular significance.

Schopper Fold for each paper tested was decreased seriously in each direction.

A soil burial of these cyanoethylated sheets was made and the results are plainly visible in Figure 17. The rag paper was not included because of lack of sample. The soil was kept at room temperature and after seven days had elapsed the samples were dug out of the soil and rinsed with water. The cyanoethylated papers withstood the treatment much better than the untreated.

Some of the cyanoethylated pulp papers were also buried and the results tend in the same direction as follows:

1271-127-A	Weyerhaeuser control	badly destroyed
1271-133-1A	1.85% N	not harmed
1271-127-D	Weyerhaeuser $Al_2(SO_4)_3$ treated	destroyed
1271-133-1D	1.85% N $Al_2(SO_4)_3$ treated	slightly destroyed

Figure 17.

Figure 18.

Effect of Cyanoethylation of Paper on Abrasion Rate

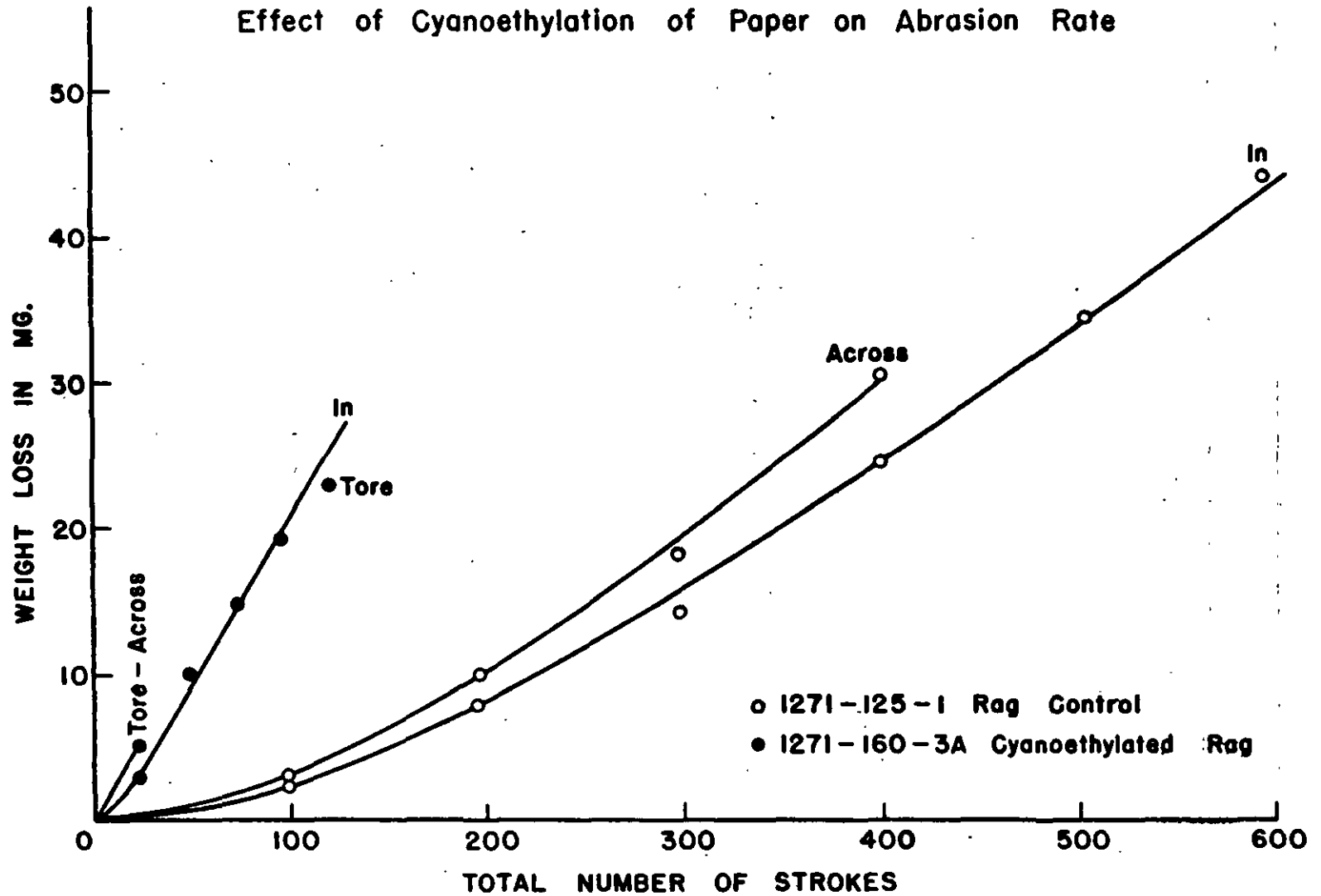

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Figure 19.
Effect of Cyanoethylation of Paper on Abrasion Rate

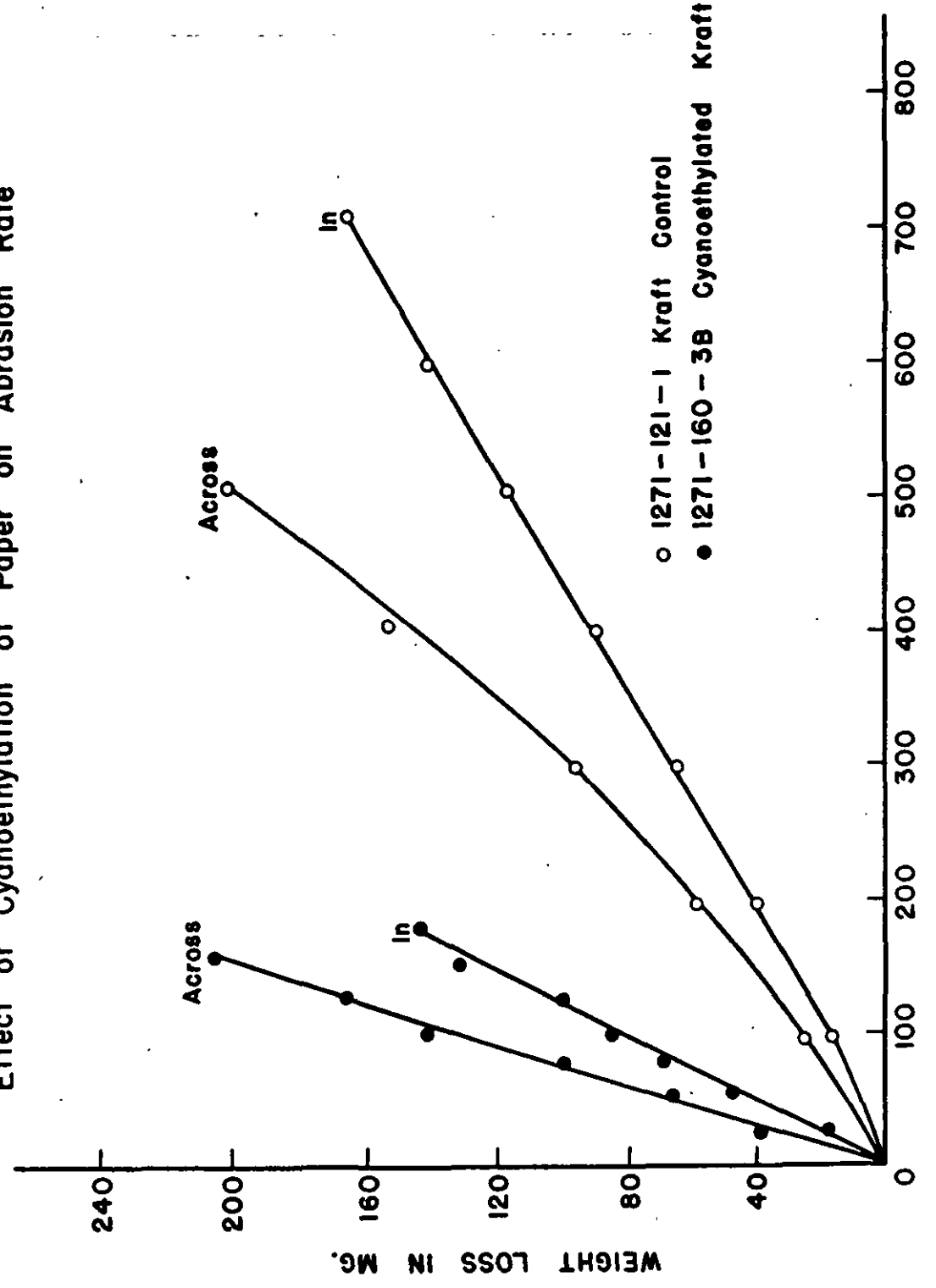
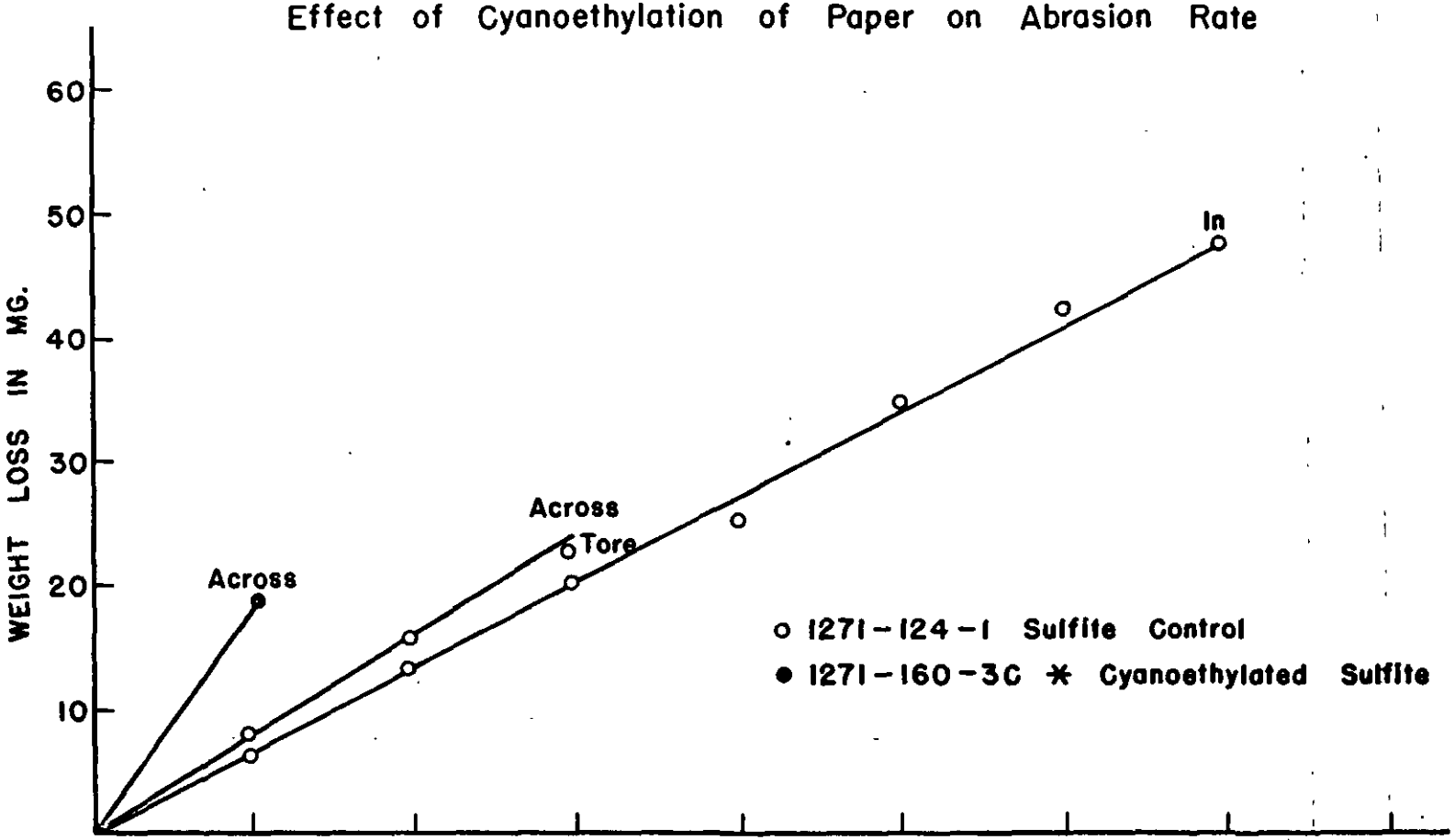


Figure 20.

Effect of Cyanoethylation of Paper on Abrasion Rate



* The In abrasion of 1271-160-3C was given as 7 mg. in 100 strokes

1271-133-1C	1.85% N NaOH treated	pin holes
1271-133-1E	50-50 mixture of Weyerhaeuser -and- 1.85% N	destroyed
1271-127-C	Weyerhaeuser NaOH treated	destroyed
1271-134-2C	5.10% N and NaOH treated	not harmed
1271-146-F	laminations Weyerhaeuser sandwiched in 5.10% N	destroyed
1271-134-2E	5.10% N + Weyerhaeuser, 50-50	destroyed

The cyanoethylated papers were the ones that withstood this treatment the best. However, for more accurate results these papers were sent to the biological department and tested for fungus resistance. Moisture and physical handling of the paper may have influenced the soil burial results to some extent.

Four samples of pulps submitted for testing to the biological department were:

1108-41-A	Weyerhaeuser control
1108-41-B	1.85% Nitrogen pulp
1108-41-C	3.43% Nitrogen pulp
1108-41-D	5.10% Nitrogen pulp.

Approximately 1 gram of each pulp was beaten in a Waring blendor and a mat 16 cm. in diameter was formed from each on a coarse sintered glass filter. The paper was tested according to TAPPI T 487. All test organisms--Chaetomium globosum, Aspergillus terreus, and Aspergillus niger--grew well on 1108-41-A. On 1108-41-B the Chaeomium globosum grew only slightly. The other two test organisms showed no growth on this sample. Pulp samples 1108-41-C and 1108-41-D did not support growth of any of the test organisms used and hence should be considered mildew resistant. Cyanoethylation has protected the paper from fungus attack. Even the 1.85% Nitrogen-containing pulp showed resistance to these organisms, although this resistance was not as complete as the higher degree of cyanoethylation.

In 1950 a patent was obtained by General Electric for cyanoethylated lignocellulose pulp in the range 0.3 to 2.8% nitrogen pulps made by cyanoethylation. (10) This paper is claimed to have higher dielectric constants than noncyanoethylated paper. In carrying out this patent, 6 to 12% NaOH solutions are used for cyanoethylation and temperatures in the range of 7°C. to 18°C.

Some work was done with this process of cyanoethylation. Cyanoethylation of Weyerhaeuser bleached sulfite by this method caused many fibers to have swelling nodes. However, at present it is uncertain that this cannot be avoided by better stirring action. An unbleached Bladel kraft was cyanoethylated by this method utilizing a screw-type stirrer, with very little swelling indicated.

Another method of cyanoethylation might be accomplished with potassium cyanide as a catalyst and acrylonitrile in the vapor state. This has already been done with viscose rayon at 35°-53°C. With this type (11) of treatment the caustic action of NaOH on the fiber might be avoided and thus it might be possible to evaluate the results of acrylonitrile alone on the paper. Of course potassium cyanide might introduce other variables than those due to caustic.

Thus far we have tried to establish trends in various directions due to cyanoethylation. However, if a trend was not apparent but only what seemed like a special case for a degree of cyanoethylation, this was also

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10. Miller, Harry F., Flowers, Ralph G., Pittsfield, Mass., assignors to General Electric Co., a corporation of New York. Application August 2, 1947, Serial No. 765,798, U.S. Patent Office 2,535,690, (Cl. 117-154), 8 claims. Patented Dec. 26, 1950.

mentioned. It should also be noted that most of our tests were on the cyanoethylation of one particular type of pulp and three types of web paper. By no means does this cover the field of cyanoethylation and it is quite possible that different types of paper, different sheet formation conditions, and different means of cyanoethylation such as changes in caustic concentration and temperature of treatment for cyanoethylation may show different and perhaps contradictory results to those which were obtained. For example--web cyanoethylation in no case showed an increase in abrasion resistance, but decreases were shown in each case. Whereas the cyanoethylated pulp, a Weyerhaeuser bleached sulfite, tended to show increased abrasion resistance; the sulfite cyanoethylated in the preformed web showed a loss of abrasion resistance. Perhaps Weyerhaeuser pulp is the only pulp that will show this type of a thing. Or, perhaps beating the pulp after the cyanoethylation treatment is what made for increased abrasion resistance. Data obtained indicated that the cyanoethylated webs were deformed and then reformed again in that the tear strength went below the untreated sheets and was of a directional nature. Perhaps the reformation of these cyanoethylated webs was of such a nature that their reformation could have been improved either by wet calendering or wet pressing.

These are a few of the questions which appear from the data thus far obtained and which probably would require a great deal of experimentation and study to answer.

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11. Nabuhiko, Kuroki (Namiva Univ., Sakai) Partial Cyanoethylation of Viscose Rayon. J. Chem. Soc. Japan Ind. Chem. Sect. 56704-7 (1953)

PROJECT REPORT FORM

PROJECT NO. 1102-10
COOPERATOR Institute of Paper Chem
REPORT NO. 17
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NOTE BOOK 1271, pp.120-129, 133-
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SIGNED pp. 20-27, 34, 39-52

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CYANOETHYLATION OF PULP AND PAPER

INTRODUCTION

Recently the partial cyanoethylation of cotton has created a new type of textile with some very desirable qualities. Some work has been done with the cyanoethylation of paper and pulp and was described in Report 16, of Project 1102-10. Since that report was written, some data has been received and is being evaluated and described in this report.

The data received for the most part concerns work which was done on cyanoethylation according to a patent issued to Miller and Flowers. The general process consists of treating a lignocellulose pulp with acrylonitrile in 6-12% caustic and from 0 to about 25°C. The reaction is stopped either by neutralization with acid or by drowning with water. (1) This is what is commonly called the one-step process in contrast to the two-step process which was often employed in the cyanoethylation of textiles. The two-step process is carried out by treating the material to be cyanoethylated with caustic and centrifuging the excess water from that material prior to the addition of acrylonitrile.

The two-step process was probably a great saving on acrylonitrile since this material reacts with water to form a dicyanoethyl ether.

(1) Miller, Harry F., and Flowers, Ralph G., U. S. patent 2,535,690 (Dec. 26, 1950).

WORK DONE AND RESULTS OBTAINED

The first attempt at cyanoethylation by the general methods described in the patent issued to Miller and Flowers was made on a Weyerhaeuser bleached sulfite pulp. The reaction consisted of the following components:

3000 g. 10% sodium hydroxide solution

157 g. Weyerhaeuser pulp

65 g. Acrylonitrile

The solution of 10% caustic was prepared and was brought to between 12 and 14°C. The pulp received in sheet form was added after being torn in pieces approximately one to three square inches in area. This was stirred for about one hour with a motor-boat type of propeller. Since there was very little movement in the slurry, a loose blade propeller was substituted and the acrylonitrile was added over a period of 15 minutes. The slurry was reacted in this condition for 3-1/2 more hours and then the caustic was neutralized. The material was jellylike and one sheet was made from this material but stuck to the screen so tenaciously that it was impossible to remove as a whole from the screen. The portion that was removed and dried on the drum drier was a parchment like paper. However, due to screen sticking, it would probably be an impossibility to make sheets from this material. When this material is wetted, it becomes very slimy. A quart of this material was saved and labeled 1108-43-A, and a photomicrograph was made of this pulp (Fig. 1). The fibers are badly blown up due to the treatment given.

Because the above conditions seemed too drastic for the fiber, the conditions were modified as follows: The acrylonitrile content was cut to one third that of the former composition. In addition, the acrylonitrile was added immediately after the pulp and allowed only a two-hour contact time

Figure 1

Cyanoethylated Weyerhaeuser pulp (1108-43-A) Magnification 100 X

prior to neutralization with acetic acid. Sheets were made from this pulp. The sheets were very soft and cottonlike. They seemed to have practically no fiber-to-fiber bonding. It was possible to blow some fiber from the sheets with one's breath almost as easily as one would blow dust from a table. Samples of the pulp were photomicrographed and are labeled 1108-43-B (Fig. 2). The sheets were labeled 1108-46-B43.

In addition to trying cyanoethylation on a bleached sulfite pulp, it was tried on a Bladel A unbleached kraft. The materials used were:

157 g. Ovendry pulp, Bladel A unbleached kraft
3000 g. 10-% Sodium hydroxide solution
65 g. Acrylonitrile

The pulp was added to the caustic followed by the acrylonitrile. The reaction was carried on for four hours at 12°C. to 12.5°C. The slurry was neutralized with acetic acid and washed in a wash box until water ran freely through the wash box cloth. That is at the start of the wash, the fiber had a tacky material which tended to stop water from running from the pulp wash box. Three such batches were prepared and combined. However, it was found that there was about 3/4 the amount of fiber, 360 g., needed to make a beater run. It appears that somewhere a great deal of pulp was lost. This loss was probably in part the dissolved resin-like material mentioned above. A batch having four times the amount of each constituent above was run and combined with the former cyanoethylated pulp. This pulp was designated 1108-45-K1. A beater run was made on this pulp and on an untreated pulp 1108-45-K. The data obtained in the beater run is in Tables I and II and is represented in Figures 3 to 5. From the figures at zero beating time one might have assumed that the cyanoethylated

TABLE I

BEATER EVALUATION DATA
Pulp Sample 1108-45-K, Bladel Kraft Control

Beating Time, min.	Schopper-Riegler Freeness, cc.	Wt. of Sheets (British) g. av.	Basis Wt., lb. 25x40/500	Caliper, inch	Apparent Density	Bursting Strength (Mullen) points	Bursting Strength (Mullen) Pt. per 100 lb.	Elmendorf Tear, g./sheet	Elmendorf Tear Factor	Baldwin-Southwark Tensile, lb./inch	Baldwin-Southwark Stretch, %
0	870	1.368	48.7	0.0057	8.5	8.4	17	73	1.50	4.7	1.3
5	865	1.335	47.5	0.0049	9.7	15.8	33	124	2.61	10.0	1.9
15	850	1.337	47.5	0.0042	11.3	32.3	68	123	2.59	17.5	2.8
30	800	1.290	45.9	0.0038	12.1	46.0	100	79	1.72	24.1	3.4
50	635	1.299	46.2	0.0035	13.2	54.7	118	65	1.41	28.3	3.6
70	395	1.294	46.0	0.0033	13.9	58.4	127	58	1.26	29.0	3.4
90	260	1.294	46.0	0.0031	14.8	60.4	131	54	1.17	31.5	3.6

Note: Institute File No. 165070.

TABLE II

BEATER EVALUATION DATA

* Pulp sample 1108-45-K1, Cyanoethylated Bladel Kraft Contaiaing 2.24% Nitrogen

Beating Time, min.	Schopper-Riegler Freeness, cc.	Wt. of Sheets (British), g.	Basis Weight, lb. 25x40/500	Caliper, inch	Apparent Density	Bursting Strength (Mullen) points	Bursting Strength (Mullen) Pt. per 100 lb.	Elmendorf Tear, g./sheet	Tear Factor	Baldwin-Southwark Tensile, lb./inch	Baldwin-Southwark Stretch, %
0	900	1.341	47.7	0.0047	10.1	32.3	68	114	2.39	12.8	3.6
5	890	1.319	46.9	0.0044	10.7	34.0	72	88	1.88	15.6	4.6
15	890	1.341	47.7	0.0041	11.6	44.4	93	68	1.43	19.9	5.1
30	845	1.379	49.0	0.0037	13.2	45.0	92	53	1.08	20.9	4.5
50	675	1.342	47.7	0.0035	13.6	44.8	94	42	0.88	22.6	4.9
70	365	1.348	48.0	0.0035	13.7	40.0	83	35	0.73	21.8	4.0

* Sheets could not be made from this pulp in the usual way by forming on screens and pressing in between blotters because of sticking. The sheets were therefore formed on nylon paper and pressed and dried still on the nylon.

Note: Institute File No. 165069

Figure 2

Cyanoethylated Weyerhaeuser Pulp (1108-43-B), Magnification 100 X

Figure 3

Freeness versus Beating Time

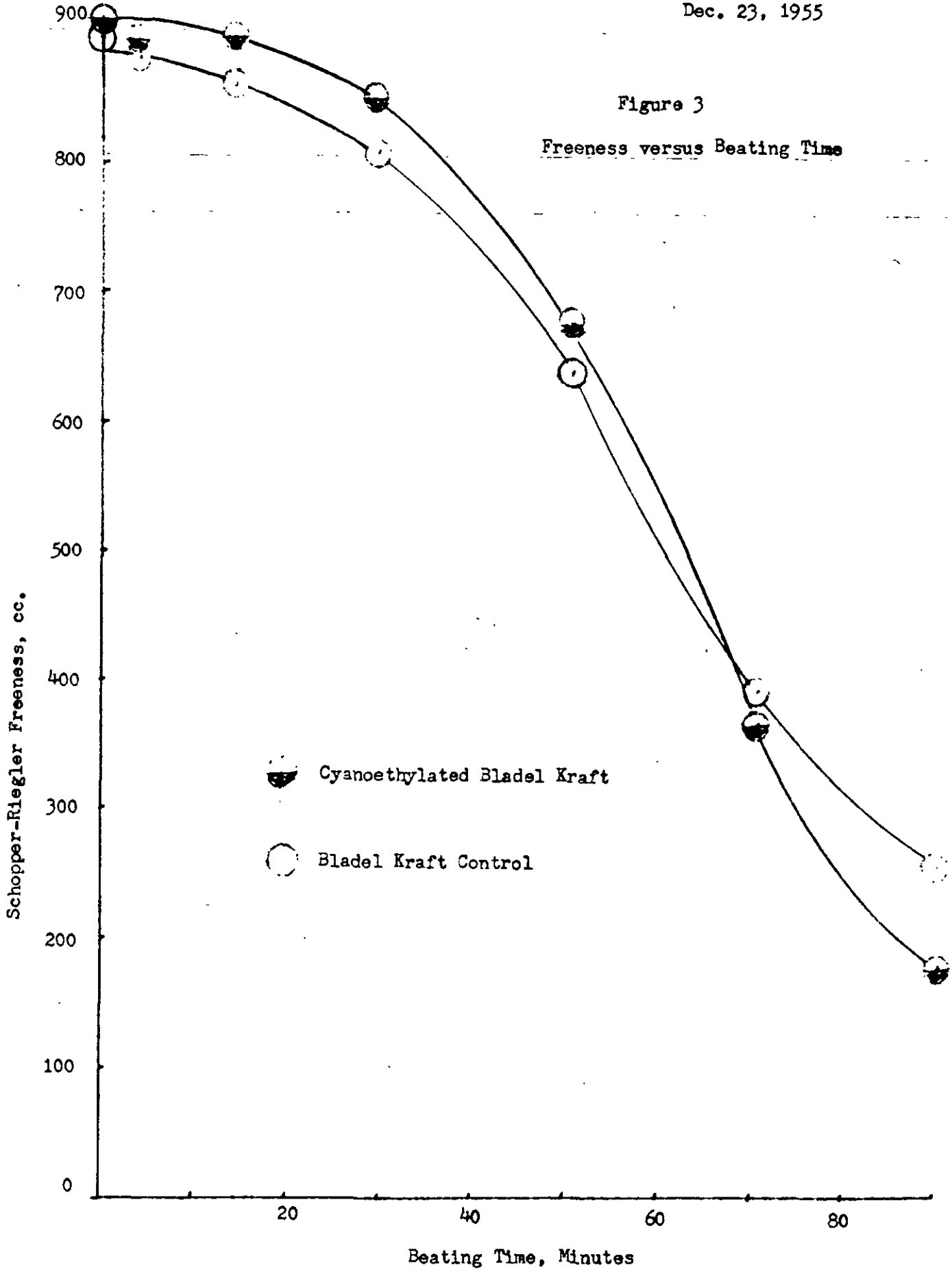


Figure 4

Beating Time versus Tear Factor

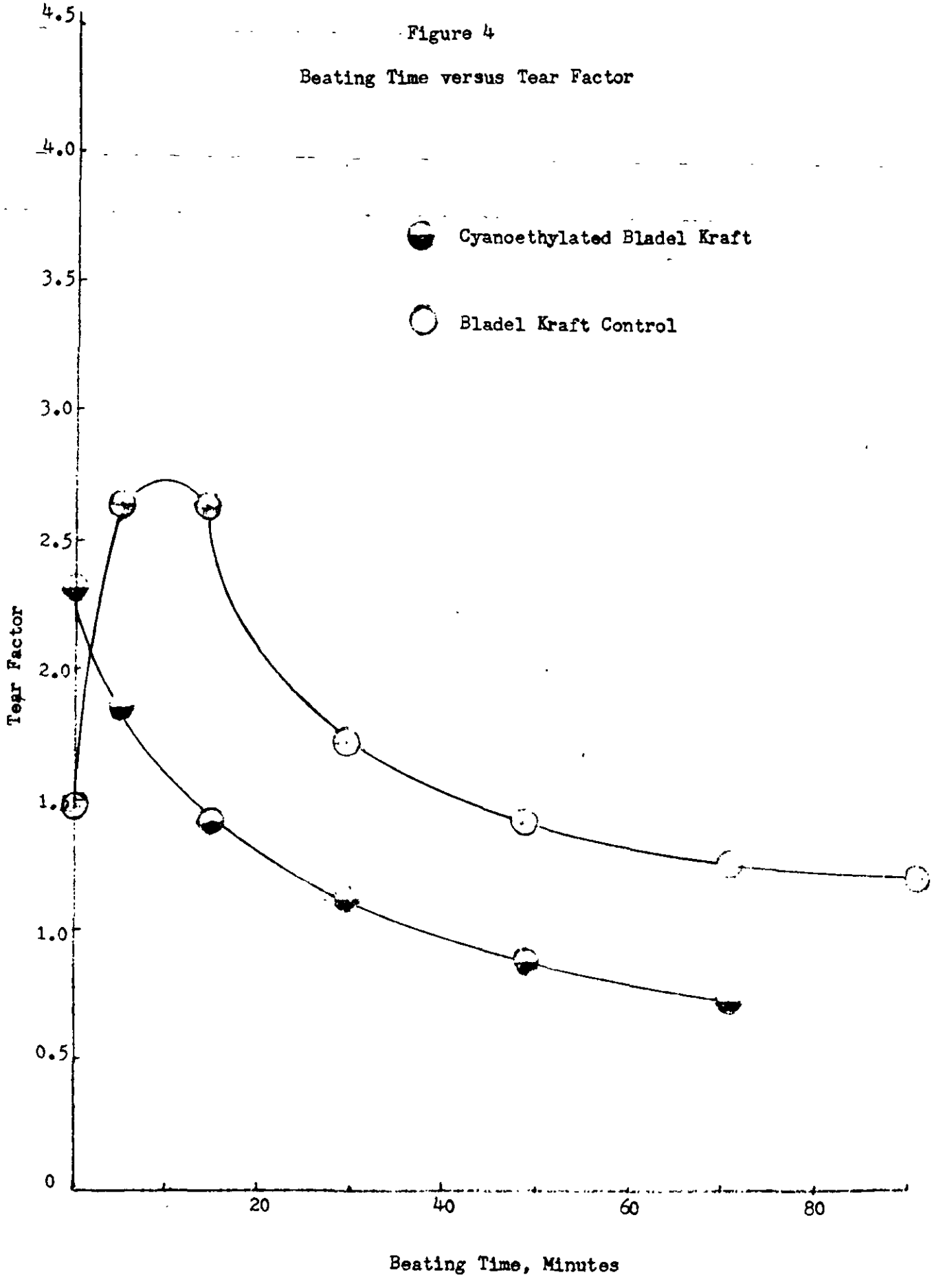
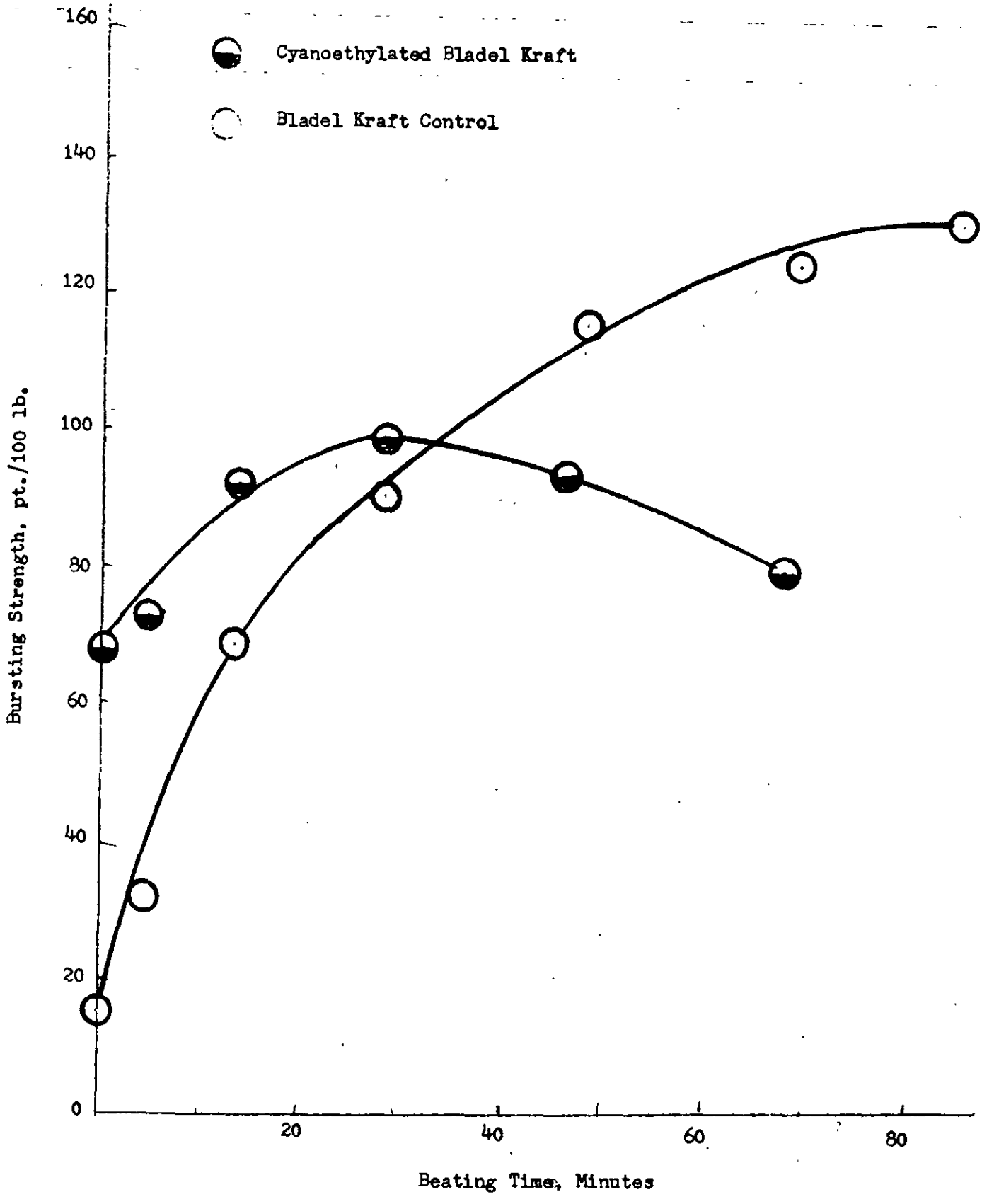


Figure 5

Beating Time versus Bursting Strength



material was stronger than the control. However, the maximum strength values obtained through the beater run were greater for the control than for the cyanoethylated kraft. If a guess were to be made as to the reason for the initial higher strength of the cyanoethylated paper, it would probably be that in the cyanoethylation of the pulp, it has already gone through part of what one might call a beater run.

In addition to the data obtained on the cyanoethylations made according to the patent mentioned above, some data has been received on some earlier work. This data concerns the Weyerhaeuser bleached sulfite pulp and those samples, mentioned in Report No. 16 of Project No. 1102-10, page 2, which were cyanoethylated by the Monsanto Chemical Company. Moisture absorption data on these samples has been obtained in order to try to compare it with hygroexpansivity values. Table III is a comparison of the data obtained. The moisture absorption data was made directly on the pulps, while the hygroexpansivity data of course was taken from sheets made from these pulps. The fact that the hygroexpansivity was higher when the per cent moisture regain was higher can be seen directly from Table III.

Some cross sectional drawings and photomicrographs of these cyanoethylated Weyerhaeuser pulps were obtained. The photomicrographs do not show vast differences. The tracings in Figures 6 and 7 seem to indicate that cyanoethylation has caused what might be termed an internal swelling. That is, instead of increasing the perimeter of the fiber the lumen has been decreased and even eliminated.

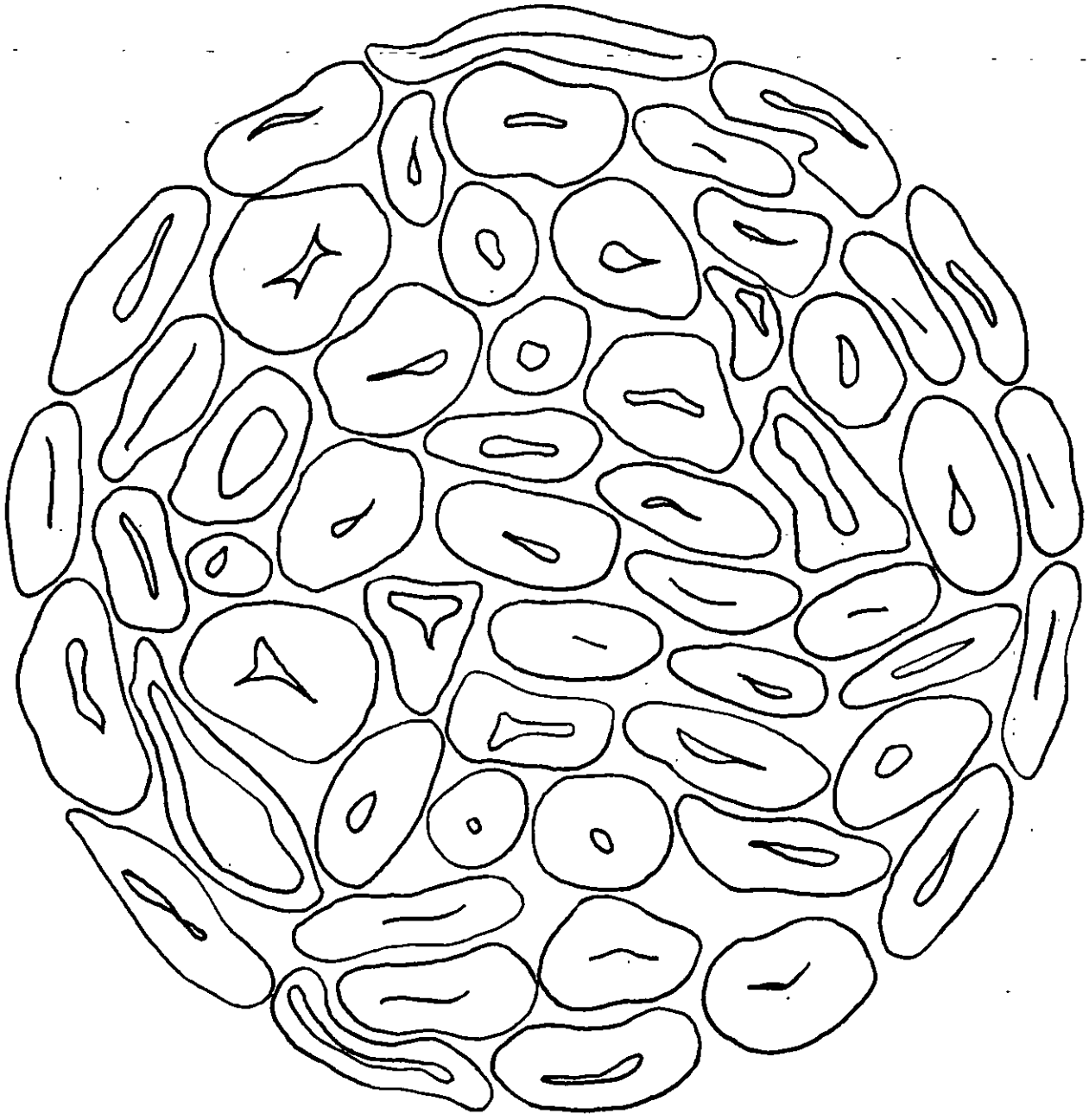
TABLE III

MOISTURE REGAIN AND HYGROEXPANSIVITY
OF CYANOETHYLATED PULP AND PAPER

Pulp Code No. and Description	Moisture Regain, % From 11.1 to 54.1% R.H.	Moisture Regain, % From 11.1 to 92.9% R.H.	Paper Code No. and Description	Hygroexpansivity, % Change from 65-50% R.H.
Weyerhaeuser Control 1108-41-A	4.6	14.8	Weyerhaeuser Control 1271-127-A	0.121
1.85% Nitrogen Pulp 1108-41-B	5.0	16.8	1.85% N Cyanoethylated Paper 1271-133-1A	0.145
3.43% Nitrogen Pulp 1108-41-C	4.1	13.0	---	---
5.10% Nitrogen Pulp 1108-41-D	3.2	11.8	5.10% N Cyanoethylated Paper 1271-134-2A	0.080

Figure 6.

0 10 20 30 40 50
μ

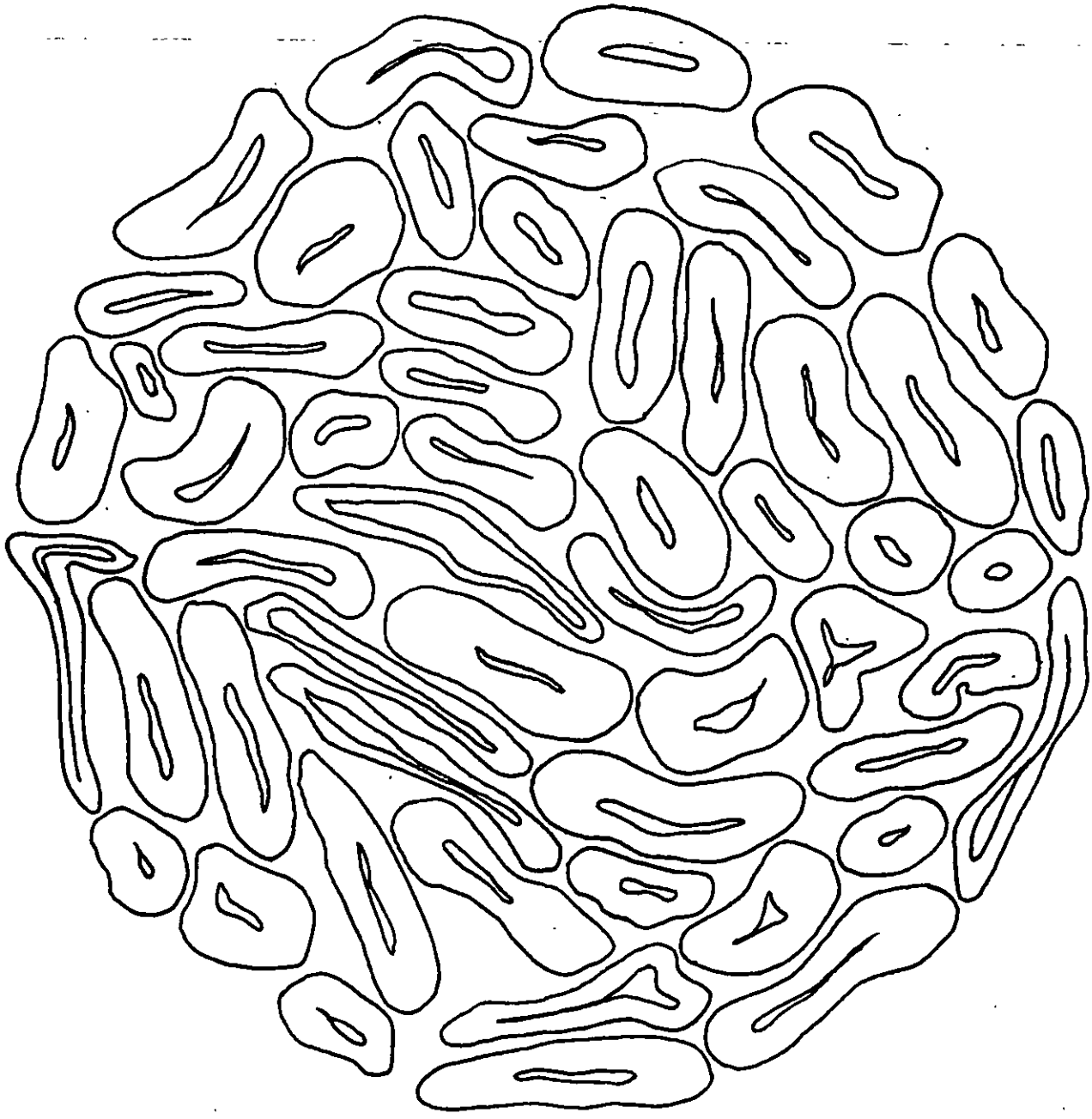


Cross Section of 8.65% N Monsanto Cyanoethylated Pulp
(1271-157-D)
Magnification 1000 X

Figure 7.

0 10 20 30 40 50

μ.



Cross Section of Weyerhaeuser Control

(1271 - 157 - A)

Magnification 1000 X

SUMMARY

Cyanoethylation seems to give paper some good qualities and some bad ones. With very few exceptions, the bad qualities imparted to the paper are found in a lowering of strength caused by cyanoethylation. One of the exceptions is found in an improved fold endurance in a Weyerhaeuser bleached sulfite cyanoethylated to 1.85% nitrogen. The strength losses were found both in cyanoethylations made on pulps from which sheets were made subsequently, and on papers which were cyanoethylated in web form.

One thing demonstrated from the work done on the Flowers and Miller patent in this report is that pulp which has been cyanoethylated should be compared for strength on the basis of a beater run. The reason for this is obvious from figures 4 and 5. That is, if one had simply made sheets from the cyanoethylated pulp without first performing a beater run and had made sheets at zero beating time, the cyanoethylated pulp would have appeared to be stronger. The results of the beater run show that the control ultimately has more strength than the cyanoethylated paper.

One of the good qualities imparted to paper by cyanoethylation is a resistance to mold and soil burial degradation. However, according to Mr. Frank Miner, Sales Manager of the Petrochemicals Department of the American Cyanamid Co., resistance of cyanoethylated textiles to soil burial degradation may be destroyed by a very small amount of hydrolysis. This may be the case with paper also; however, no paper was deliberately hydrolyzed and tested for soil burial resistance.

There was some evidence of heat degradation and abrasion resistance caused by cyanoethylation. However, these results were specific to papers made from a cyanoethylated Weyerhaeuser bleached sulfite pulp. Papers cyanoethylated in web form did not show this type of resistance.

Cyanoethylated papers have different dyeing characteristics than noncyanoethylated papers. For example, in a mixture of Calcomine Blue DR and Calcomine Scarlet 3B, the more cyanoethylated the paper--the more red it picks up, and the less cyanoethylated--the more blue it picks up. By visual comparison, the degree of dyeing or dye pickup seems to be greater for the cyanoethylated papers.

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PROJECT REPORT FORM

PROJECT NO. 1102-10
COOPERATOR I.P.C.
REPORT NO. 18
DATE January 22, 1962
NOTE BOOK --
PAGE -- TO --
SIGNED Frans Vaurio
Frans Vaurio
Don Ford
Don Ford

Copies: Files
Dr. Howells
Special Processes File

USE OF FUSIBLE POWDERS TO COAT MOLDED PULP CONTAINERS WHILE WET

This report covers the work done on the evaluation of a process for coating molded pulp containers with fusible powdered polymers. This is an extension of the work done for Project 2305 to explore some ideas that arose after the completion of that particular project.

In order to simulate the construction of a molded pulp item, newsprint in the form of damp sheets of St. Lawrence newsprint were used underneath the damp handsheets. Four sheets of newsprint, basis weight 54.18 grams per square meter, were used for each handsheet. This newsprint had been soaked in tap water and then pressed for 5 minutes at 190 on the gauge.

Attempts to use a vibrating screen to apply the powder were unsatisfactory. However, an edge activated screen may still bear further consideration as a means of sifting a uniform layer of powder onto paper.

The Martinson knife coater was used to apply the various fusible powders to the damp handsheets. The knife opening on the Martinson coater was set at 0.050 inch from the plate.

A small mound of powder was placed at one edge of the handsheet and the handsheet with four layers of newsprint underneath was pulled through the coater by hand.

The paper coated with powdered polymer was then pressed in the cup press between aluminum press plates (see Project 2305). The aluminum plates were

held at a temperature of 400°F with the use of variable voltage transformers. A sheet of Teflon was placed over the coating of powder to permit release of the coating. The sheets were pressed at 50 p.s.i. for 20 seconds. The portion underneath the heated cauls was fairly dry after this pressing time. The outer portion remained damp and was cut off when dry. The coated sheets tended to curl on standing. The results are given in Table I.

This brief study indicates that powdered polymers can be applied to wet paper with a knife-type coater provided the powdered polymers are of a free flowing type. Very fluffy, highly electrostatically charged powders such as the Microthene polyethylene powder refused to flow under the blade of a knife coater and tended to push ahead of the knife leaving uncoated areas. Previous work on Project 2305 indicated that a fluffy polyethylene powder adhered better when electrostatically sprayed than did the readily flowable types of polymer powders.

Although the title of this project refers to molded pulp containers it must be pointed out that the present work is merely to find a method for applying powdered polymers for experimental purposes. Other means would be required for introducing a uniform coating of powdered polymer into the cavity of a molded pulp container in a commercial process. Mr. Vaurio's invention record suggesting the use of a heated mandril and a fluid powder bed for applying powdered polymers to molded containers may be considered. This technique, however, has not been tried experimentally.

The best results were obtained with Koppers Polystyrene Fines - No. 100, Spencer Poly-Eth 2318, Spencer Poly-Eth 2309, and Marlex 6009. The Dow X-3314 gave colorless, clear, smooth fused films but there was a slight tendency for the film to fracture when distorted.

TABLE I

POWDERED POLYMER COATINGS

Code No.	Polymer Type	Basis Weight Grams per sq. meter	Coating Weight Grams per sq. meter	Comments
1411-72-1	Koppers Polystyrene Fines No. 100	234.62	119.51	Smooth, clear, colorless fused coating
1411-72-2	Vinylite VYNH	169.40	54.29	Tan, smooth, fused coating
1411-72-3	Vinylite VYNS	199.33	84.22	Light tan, smooth, fused coating
1411-72-4	Microthene (polyethylene)	--	--	Clear, smooth, fused coating. However, powder would not spread well; amount of coating too small to measure
1411-72-5	Geon 435	221.04	105.93	Light brown, smooth, fused coating
1411-73-1	Vinylite VAGH	164.44	49.33	Dark brown to black, film destroyed in black areas, smooth, fused coating in center. Pressing time 1 minute.
1411-73-2	Vinylite VAGH	165.80	50.09	All of drab color. Bubbled appearance over large areas. Feels smooth
1411-73-3	Vinylite VAGH	166.08	50.97	Green/grey color. Some bubbled areas. Unfused areas underneath. Smooth, fused surface. Pressing time 10 seconds.
1411-73-4	Geon 400x29	240.91	125.80	Light brown. Bubbled along edges. Surface is fused and smooth.
1411-73-5	Spencer Poly-Eth 2318	165.73	50.62	Smooth, colorless, fused surface
1411-74-1	Formvar 7-95S	186.62	71.51	Waffled, rough surface. Powder did not spread well under knife; caused tearing
1411-74-2	Atlac 382	215.36	100.25	Mottled surface, colorless. Extensive migration of the resin into the paper to cause newsprint to stick to liner sheet.
1411-74-3	Lemac 7	214.83	99.72	Surface mottled. Some blistering of surface. Colorless. Extensive migration of the resin into the paper
1411-74-4	Diamond PVC-30	284.14	169.03	Light purple. Blistered surface
1411-74-5	Spencer Poly-Eth 2309	180.14	65.03	Colorless, smooth, clear, fused film
1411-75-1	Dow X-3314	167.44	52.33	Colorless, clear, smooth, fused film. Tendency for film to fracture on first bending.
1411-75-2	Marlex 6009	198.71	83.60	Colorless, clear, smooth, fused film.

NOTE: Pressing time 20 seconds except where noted. Temperature 400°F. Basis weight of handsheet 115.11 grams per square meter. Thickness of the powdered material was approximately 0.022 inch.

There was no attempt to study the waterproofness or greaseproofness of the coatings as produced. This may be considered as a part of future work.

The coating weights applied in this study were all heavier than the 22 grams per square meter found for a typical hot drink paper cup.

The exploration of the limits of this coating technique will require further work in order to have a basis for considering the economics of this technique as compared with the application of a free film of the polymer.